THE SYNTHESIS AND CHARACTERIZATION OF BINUCLEAR COPPER(I) COMPLEXES AS MODELS FOR PROTEIN ACTIVE SITES

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ABSTRACT

A series of coordinatively unsaturated copper(I) complexes of binucleating nitrogenous ligands have been examined as potential models for protein active sites. The first complex discussed is derived from the ligand N, N, N′, N′-tetrakis(2-pyridylmethyl)-ethylenediamine (TPEN). The binuclear copper(I) complex $Cu_2(TPEN)^{2+}$ reversibly binds two equivalents of carbon monoxide, giving an adduct which displays a pair of CO stretching absorptions at 2097 and 2107 cm^{-1}. Both $Cu_2(TPEN)(BF_4)_2$ and its carbonyl adduct have been examined by single-crystal X-ray diffraction. Each copper atom of $Cu_2(TPEN)^{2+}$ is bound in a highly asymmetric environment, with an intramolecular copper-copper separation of 2.78Å. In the carbonyl adduct the metal-ligand bonds have rearranged, each copper has assumed a pseudotetrahedral geometry, and there is no longer any direct metal-metal interaction.

Another complex, $Cu_2(CHXNpy)^{2+}$, has been prepared with a ligand analogous to TPEN, but with trans-1,2-cyclohexanediamine substituted for ethylenediamine. A second cyclohexanediamine-based ligand, CHXNbim, has been prepared which contains four benzimidazole groups rather than pyridine. Both $Cu_2(CHXNpy)^{2+}$ and $Cu_2(CHXNbim)^{2+}$ exhibit temperature dependent proton magnetic resonance spectra. The fact that fast exchange is observed only well above room temperature, in spite of the high lability of copper(I), is attributed to the sterically constrained nature of the ligands. Like $Cu_2(TPEN)^{2+}$, $Cu_2(CHXNpy)^{2+}$ forms a dicarbonyl adduct, but it is

of lower stability. The benzimidazole complex $Cu_2(CHXNbim)^{2+}$ does not react with carbon monoxide and reacts only slowly with oxygen. Furthermore, unlike $Cu_2(TPEN)^{2+}$ and $Cu_2(CHXNpy)^{2+}$, $Cu_2(CHXNbim)^{2+}$ shows no tendency to disproportionate. This high stability is likely due to a combination of steric and electronic factors, which are discussed.

Finally, a series of complexes having different xylylene "backbones" have been synthesized and examined. Each ligand contains four biologically relevant imidazole groups. All of the complexes react rapidly with carbon monoxide and oxygen (irreversibly in the latter case). In contrast with another known xylylene-based complex containing pyridine groups, the reaction with oxygen occurs without ligand hydroxylation. Factors which could contribute to the reactivity difference are discussed.

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CHAPTER 1

Introduction

Proteins that contain copper occur in a wide variety of both plants and animals, including humans. Understanding the essential role played by the metal is important in gaining a fuller understanding of a number of biological processes. Such knowledge could have much wider-reaching implications regarding the chemistry of copper complexes in general, however; many of the properties displayed by copper ions in proteins have either never or only recently been observed for the metal outside of a protein environment.

In a number of copper-containing proteins the metal ions have been found to occur in pairs in some or all of the active sites. These binuclear sites generally have certain unique spectral and other properties in common, and a direct interaction with molecular oxygen (dioxygen) is usually implicated as part of their physiological function. Although other aspects of their behavior may vary, these sites are sometimes grouped together under the designation of "type 3" copper centers.[1,2] Proteins which contain such sites include hemocyanin, tyrosinase, laccase, ceruloplasmin, and ascorbate oxidase. The first of these, hemocyanin, serves as the oxygen carrier in the blood of various arthropods and molluscs.[3,4] Tyrosinase, widely distributed among plants and animals, including humans, catalyzes both the o-hydroxylation of monophenols (cresolase activity, eq. 1) and the two-electron oxidation of o-diphenols (catecholase activity, eq. 2).[5-7]

$$\text{Monophenol} + O_2 \rightarrow \underline{o}\text{-quinone} + H_2O \quad (1)$$

$$2\ \underline{o}\text{-Diphenol} + O_2 \rightarrow 2\ \underline{o}\text{-quinone} + 2H_2O \quad (2)$$

Laccase and ascorbate oxidase, in plants, and ceruloplasmin, in mammals, all catalyze the multielectron reduction of oxygen to water (eq. 3) in conjunction with the oxidation of various substrates.[8-10]

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad (3)$$

(Ceruloplasmin appears to have other functions as well.[10]) In addition to one or more type 3 sites, each of these last three proteins ("blue oxidases") contains other copper centers (types 1 and 2).

Perhaps the most intriguing property of binuclear copper sites is their apparent ability to form dioxygen adducts. This ability is clearly evident in the case of hemocyanin and tyrosinase, both of which bind oxygen reversibly in their reduced forms with a stoichiometry of one molecule of oxygen per two copper ions.[11-13] The resulting oxyhemocyanin and oxytyrosinase have quite similar spectral features.[13] Experiments with oxidized (resting) Rhus vernicifera (lacquer tree) laccase indicate that it forms a stable, high-affinity complex with peroxide, probably at the type 3 site, that may be similar to the dioxygen adducts of hemocyanin and tyrosinase.[14]

Other properties which, together with the interactions with dioxygen, serve to distinguish type 3 copper from other types of active sites include various unusual spectral, magnetic, and electrochemical properties. The electronic absorption spectrum of oxyhemocyanin is dominated by intense bands at ~ 600 nm ($\epsilon \approx 1000\ M^{-1}\ cm^{-1}$) and

~350 nm ($\epsilon \approx 20,000\ M^{-1}\ cm^{-1}$).[15] The spectrum of oxytyrosinase shows corresponding features (although with some differences).[13,16] The spectra of the blue oxidases show a number of absorptions, most of which are associated with type 1 copper; however, a band at 330 nm ($\epsilon \approx 4000\ M^{-1}\ cm^{-1}$) is associated with the type 3 center.[9] In contrast to the above, simple inorganic copper(II) complexes typically show a single broad, relatively weak ($\epsilon < 100\ M^{-1}\ cm^{-1}$) band in the 500 to 900 nm region.[15,17] Furthermore, type 3 centers exhibit no detectable electron paramagnetic resonance (EPR) absorptions, even when the copper ions appear to be in a +2 oxidation state, as in oxy or met (oxidized) hemocyanin or resting tyrosinase or blue oxidases.[9,18-20] (In the case of the blue oxidases the observed signals are of sufficient intensity to account only for the non-type 3 copper centers.[9,20]) Although the lack of an observable EPR signal could be accounted for in a variety of ways, temperature-dependent magnetic susceptibility measurements have shown in several cases that the binuclear sites are, in fact, diamagnetic.[19,21-23] (Precise measurements on laccase and ceruloplasmin indicate that the susceptibility is quantitatively accounted for by the type 1 and type 2 centers.[22,23]) Such diamagnetism for a pair of copper(II) ions would require strong antiferromagnetic coupling ($J > 500\ cm^{-1}$).[22]

Type 3 centers whose oxidation-reduction properties have been examined have been found to act as cooperative two-electron acceptors (i.e., both ions are reduced at the same potential). Reduction potentials measured by means of oxidation-reduction titrations are 0.36, 0.43, and 0.78 V (vs. nhe) for the binuclear centers of tyrosinase,[19]

Rhus laccase,[24, 25] and Polyporus laccase,[25] respectively. The redox properties of hemocyanin have not been reported. This behavior is unusual compared to that of most simple copper complexes, in which reduction commonly occurs at considerably lower potentials and, in cases involving two interacting metals, in one-electron steps at different potentials.[26-31] The high reduction potentials in proteins are indicative of a high stability for the +1 oxidation state of copper relative to the +2 state.

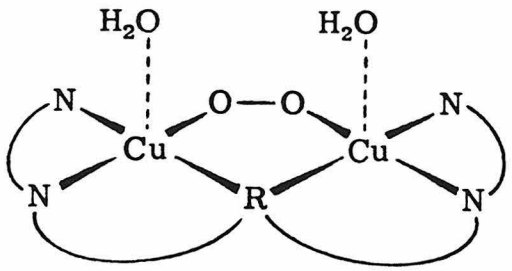
In the search to determine what structural factors and types of ligation are responsible for the unique behavior of binuclear copper active sites, studies on the proteins themselves have thus far provided only limited information. X-ray crystallographic studies are under way which will eventually yield a more direct picture of the active site.[15] However, it will still be necessary to supplement this with other studies to provide a complete understanding of the site's properties. Another approach that can give insight in this regard is to study relatively simple copper complexes that can potentially mimic various aspects of the site's behavior. Such complexes are the concern of this thesis.

In designing model complexes it is appropriate to make use of what information is available regarding the structure of binuclear copper centers. This information has recently been reviewed.[15, 32] The active site of hemocyanin has been studied in the greatest depth, and the structure that has been formulated for it in the oxygenated state is probably the most accurate for any binuclear copper site. Studies on the type 3 sites of the blue oxidases have been hampered by

the presence of other copper centers, but a structure has been suggested for the former sites that is similar to that of hemocyanin.[9]

Resonance Raman spectral studies indicate that the dioxygen in oxyhemocyanin is bound as peroxide, and in such a way that the two oxygen atoms are equivalent.[33-35] The optical absorption spectrum has been interpreted as indicating end-to-end bridging coordination between the two copper ions.[15,18] With regard to other ligands, a number of results from ESCA,[36] EXAFS,[37-39] and other spectroscopic[18] and chemical[40,41] studies show that sulfur is not a strong donor atom at the hemocyanin active site. Instead, resonance Raman,[42,43] EXAFS,[37-39] and EPR[44] studies, as well as acid-base titrations[45,46] and photochemical studies,[47,48] all point to the presence of several imidazole groups (histidine) at the active site. In addition, studies on hemocyanin derivatives[18] indicate the presence of another endogenous bridging ligand, which may be phenoxide, alkoxide, or simply hydroxide (or oxide). Superexchange coupling via this ligand and possibly peroxide would provide an explanation for the diamagnetism of oxyhemocyanin.

On the basis of the above and chemical and spectroscopic studies of a series of hemocyanin derivatives, Solomon and co-workers have suggested $\underset{\sim}{1}$ as a "spectroscopically effective" structure for the active site in oxyhemocyanin.[15,18,49] The coordination geometry is tetragonal, and each copper is bound to at least two imidazole nitrogens, a bridging peroxo group, and a bridging endogenous ligand (R), with an exchangeable axial position for associative ligand displacement



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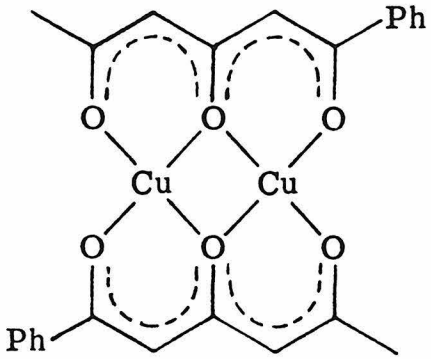
reactions. It is acknowledged that the actual active site is undoubtedly highly distorted. Studies conducted on an analogous series of derivatives of tyrosinase have shown that its active site is very similar to that of hemocyanin.[16] It has been suggested that tyrosinase might be viewed as having a hemocyanin active site with high accessibility for organic substrates. The activity of tyrosinase has been explained in terms of the effective structure 1.[16]

Less information is available about the deoxy than the oxy form of hemocyanin due to the inapplicability of electronic absorption and EPR spectroscopies to the d^{10} copper(I) ion. However, two different structures have been proposed for the deoxy site on the basis of EXAFS data. In one of these, suggested by Spiro and co-workers,[37] the copper(I) ions are separated by 3.39Å, but are not bridged. It is suggested that each ion is coordinated to three imidazole groups (although the EXAFS results are actually more consistent with two). Hodgson and co-workers have interpreted their data to indicate that the copper(I) ions are separated by more than 4.5Å, with each coordinated to two imidazole nitrogens.[39] Both groups agree that the coordination

changes considerably on oxygenation to give a structure similar to 1 with a copper-copper distance of about 3.6Å.[37,38] (Hodgson et al. suggest an approximately square-planar coordination for Cu(II) on the basis of absorption edge data, while Spiro et al. favor the presence of a third axial imidazole group on the basis of their resonance Raman data[43] and other information.)

Studies of model complexes have already helped to some extent in formulating the picture of the type 3 active site. Strong antiferromagnetic coupling, sometimes leading to diamagnetism, has been observed in various binuclear copper(II) complexes.[50-60] It is partly on the basis of these results that the endogenous bridging ligand is suggested to be phenoxide, alkoxide, or hydroxide.[61] Compound 2 and related species have been reported not only to be diamagnetic, but to undergo



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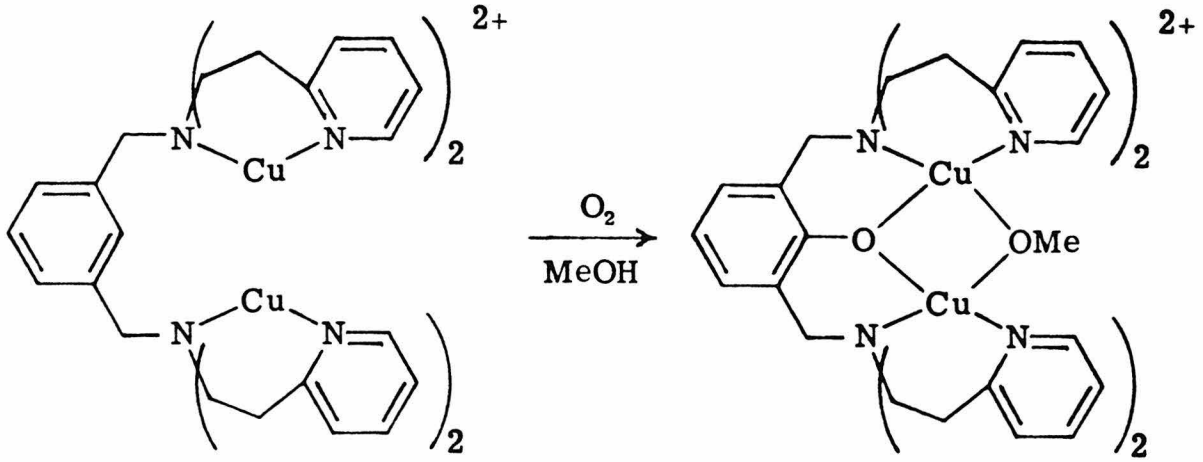
reduction in a one-step, two-electron process (although at potentials much lower than type 3 copper).[59,60,62] Copper complexes have been reported whose reduction potentials are comparable to those of

proteins, but in many cases sulfur ligands are involved which probably do not provide an appropriate representation of the environment at the type 3 site.[26, 30-32, 64-66] Work in our laboratories has resulted in binuclear complexes whose reduction potentials approach those found for proteins and which contain only nitrogen and oxygen donor atoms (vide infra).

A variety of copper-catalyzed oxidation and oxygenation reactions have been reported, some of which might be considered as models for the action of tyrosinase or ascorbate oxidase.[67] However, in many cases the nature of the catalytic species is not clear, partly because the ligands involved are not conducive to a well-defined coordination environment. A possible exception to this is provided by the binuclear copper(I) complex 3, which resembles some of the complexes reported in this thesis. Although it is not a catalytic reaction, the recently described autoxidation of 3 bears similarity to the activity of tyrosinase in that it results in hydroxylation of a benzene ring.[68]



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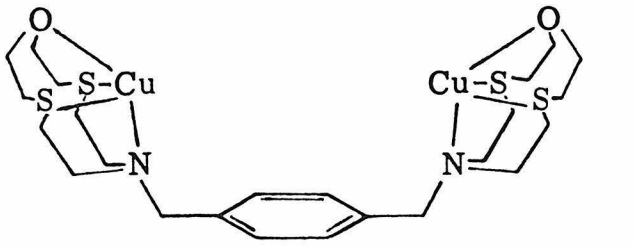
Some results have appeared which indicate that a few complexes may mimic the oxygen-carrying behavior of the binuclear copper site. The copper(I) complexes 4 and 5 have been found to undergo various changes that appear to be at least partially reversible after exposure to oxygen, in the solid state in the case of 4[69] and in both the solid state and solution in the case of 5.[70,71] The results that have been reported do not conclusively indicate the formation of stable dioxygen adducts,



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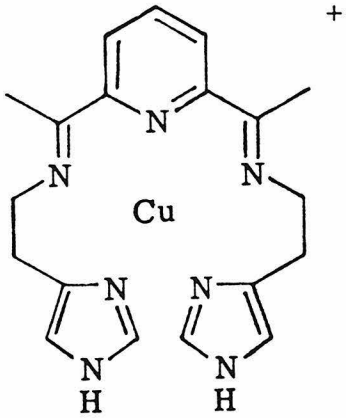

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however. For example, in neither case has evidence been presented for an intact oxygen-oxygen bond, such as an infrared or Raman O-O stretching absorption.

The chapters which follow in this thesis present a series of binuclear copper(I) complexes designed to serve as potential models for the reduced type 3 active site. While many complexes containing two copper(II) ions are known, the number of well-characterized binuclear copper(I) complexes is rather limited. This is especially true of those having only nitrogen or oxygen donor atoms and low coordination

numbers (two or three), as in the structure suggested for the deoxyhemocyanin site.[72-79] There is a need for study of such complexes in order to determine what factors are responsible for the high stability and unusual reactivity of copper(I) in proteins.

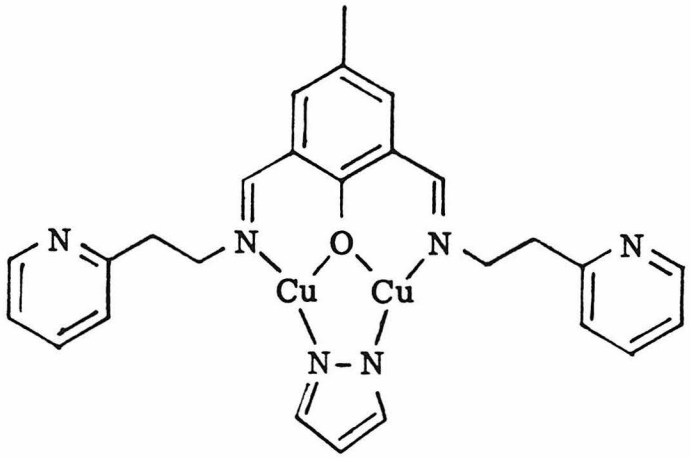
In addition to a desire to provide ligation similar to that indicated for proteins, other general considerations have been involved in the design and study of the complexes to be discussed. The following factors have been stated to be important for producing dioxygen-carrying activity in a transition metal complex:[80, 81]

> The complex should have filled π-bonding orbitals of intermediate energy to allow partial but not complete electron transfer from the metal atom to O_2.
>
> The coordination number and/or stereochemistry of the dioxygen adduct should be typical for the reduced state of the central atom but atypical or impossible for the oxidized state.
>
> The reduced complex must be able to increase its coordination number or have at least one very weakly bound ligand.
>
> The formation of $HO_2^{\bullet}$ or H_2O_2 should be suppressed.

Being a d^{10} metal, copper(I) certainly has filled orbitals that can engage in π-bonding with O_2. The second and third factors indicate that the copper(I) complex should be two-, three-, or possibly four-coordinate and that adduct formation should produce a geometry such as trigonal or tetrahedral that is favorable for copper(I). Geometries such as octahedral, square pyramidal, or square planar, which favor copper(II) (due to ligand field stabilization), should be avoided according to the

second criterion.[26-28, 82-84] The +1 oxidation state is also stabilized by "soft", π-acidic ligands. In a biological context, this could mean aromatic nitrogen or sulfur ligands, but the latter have not been used for reasons that have already been made clear. Because copper is labile in both the +1 and +2 oxidation states, the use of multidentate binucleating ligands is desirable in order to maintain control over the coordination in solution. The last factor in the above list indicates that protic solvents and ligands with acidic protons should generally be avoided if reversible oxygenation is desired.

These criteria were applied in the design of complex 6, originally synthesized by R. P. Kreh in our laboratories. This complex was intended as a modification of 7[28] that would give greater



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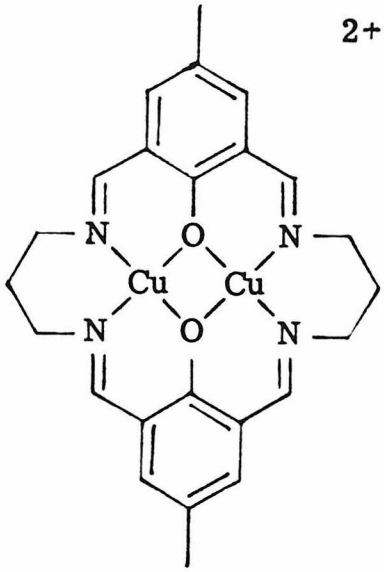

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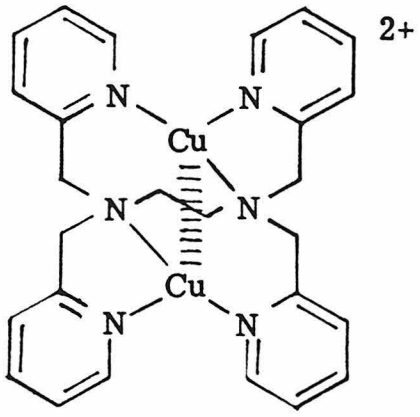
stability to the +1 oxidation state of copper. It had been assumed that each copper(I) ion would adopt a pseudotetrahedral geometry, with

bonds to three nitrogens and a bridging oxygen. However, an X-ray crystallographic analysis, performed by the present author, showed that the pyridine groups are not coordinated and that the metals are bound in an unusual T-shaped geometry. The analysis further revealed the presence of an intermolecular copper-copper interaction in the solid state. On the basis of this structure Kreh synthesized a series of analogous compounds in which the pyridylethyl groups were replaced by substituents containing no donor atoms. Some of these compounds exhibited quasi-reversible oxidation at potentials approaching those for proteins. These results are presented in detail in the Appendix.

Complex 6 and its analogues are evidently not suited to the formation of adducts. Although they appear to have open coordination sites in solution as well as the solid state, they do not react with carbon monoxide. Furthermore, the open sites face away from one another, which would not seem conducive to the formation of adducts with bridging ligands (such as dioxygen). Kreh attempted to synthesize compounds similar to 6 without the pyrazolate group, but was unable to isolate them in pure form.[63]

Complex 8 represents a somewhat different approach to the problem of forming a coordinatively-unsaturated binuclear copper(I) compound. Again, X-ray diffraction studies revealed a somewhat unexpected structure, which includes a direct intramolecular copper-copper interaction. Unlike 6, complex 8 does readily form adducts, such as the dicarbonyl 9. An X-ray analysis of 9 showed that major structural rearrangement occurs to give a more conventional pseudo-tetrahedral geometry about each copper ion. These results are



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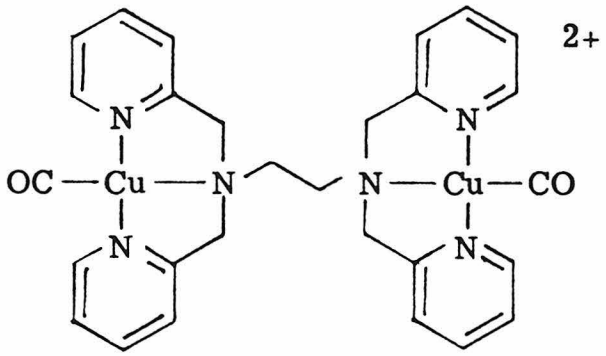

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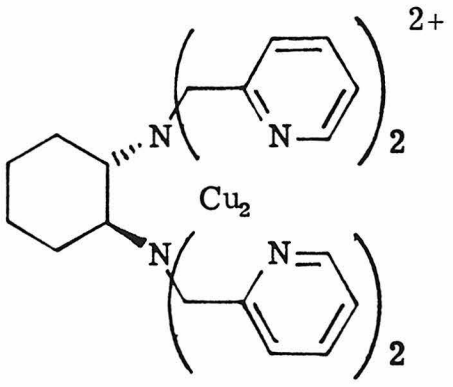
presented in Chapter 2. The syntheses of 8 and 9 were originally performed by Kreh and the X-ray study of 9 by M. McCool.

Complexes 10 and 11, discussed in Chapter 3, incorporate ligands with greater steric constraints. These compounds were



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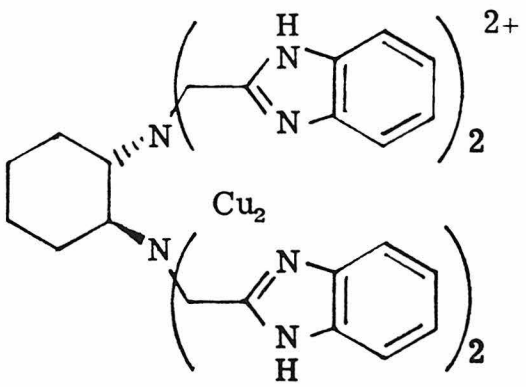

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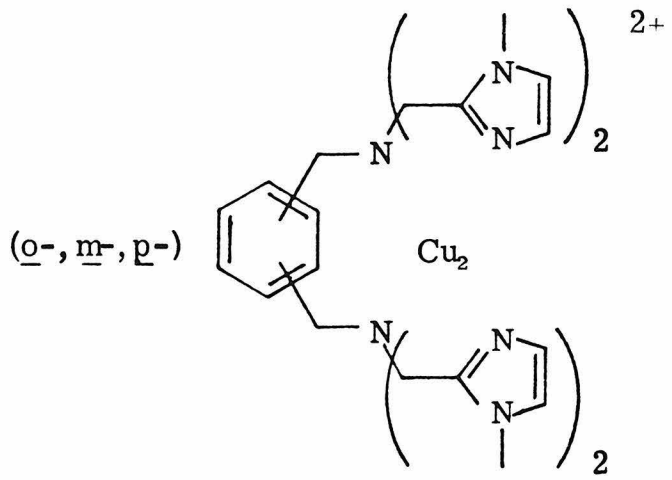
prepared in an effort to promote interaction of both copper ions with a single small molecule (such as CO or O_2), and to compare the effects of coordination by two different types of nitrogenous heterocycles. Complex 10 forms a dicarbonyl adduct which is somewhat unstable, while 11 is generally unreactive and exhibits much greater stability than 10.

Finally, a series of complexes have been synthesized which represent somewhat of a compromise among the complexes of Chapters 2 and 3 in terms of ligand flexibility. These complexes, depicted schematically as 12, employ biologically relevant imidazole groups and various xylylene "backbones". These are presented in Chapter 4.



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CHAPTER 2

The Synthesis and Structure of (N, N, N′, N′-Tetrakis(2-pyridylmethyl)ethylenediamine)dicopper(I) and its Dicarbonyl Adduct

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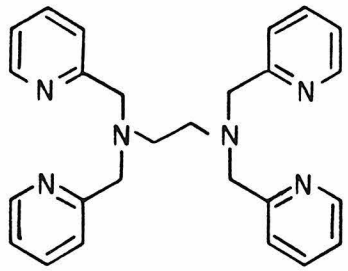
Introduction

Copper(I) complexes show a variety of coordination environments ranging in coordination number from two to five.[1,2] The number of ligands bound to the univalent metal seems to be influenced greatly by both the chemical nature of the ligands and the geometry they impose. We recently reported a series of binuclear copper(I) complexes which are three-coordinate in the solid state and display an additional intermolecular copper-copper interaction (shorter than the intramolecular separation between metals).[3] These complexes appear to be three-coordinate in solution as well, with no intermolecular interaction. In spite of the presence of an available (fourth) coordination site at each metal, the compounds are unreactive toward ligands such as pyridine and carbon monoxide. (See Discussion section.)

In contrast, a stable carbon monoxide adduct is formed with the binuclear copper(I) complex derived



TPEN

from the ligand N, N, N′,N′-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN). To facilitate comparison of the systems, complete crystal structural analyses of both $Cu_2(TPEN)(BF_4)_2$, 1, and its dicarbonyl adduct, $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2, have been undertaken.

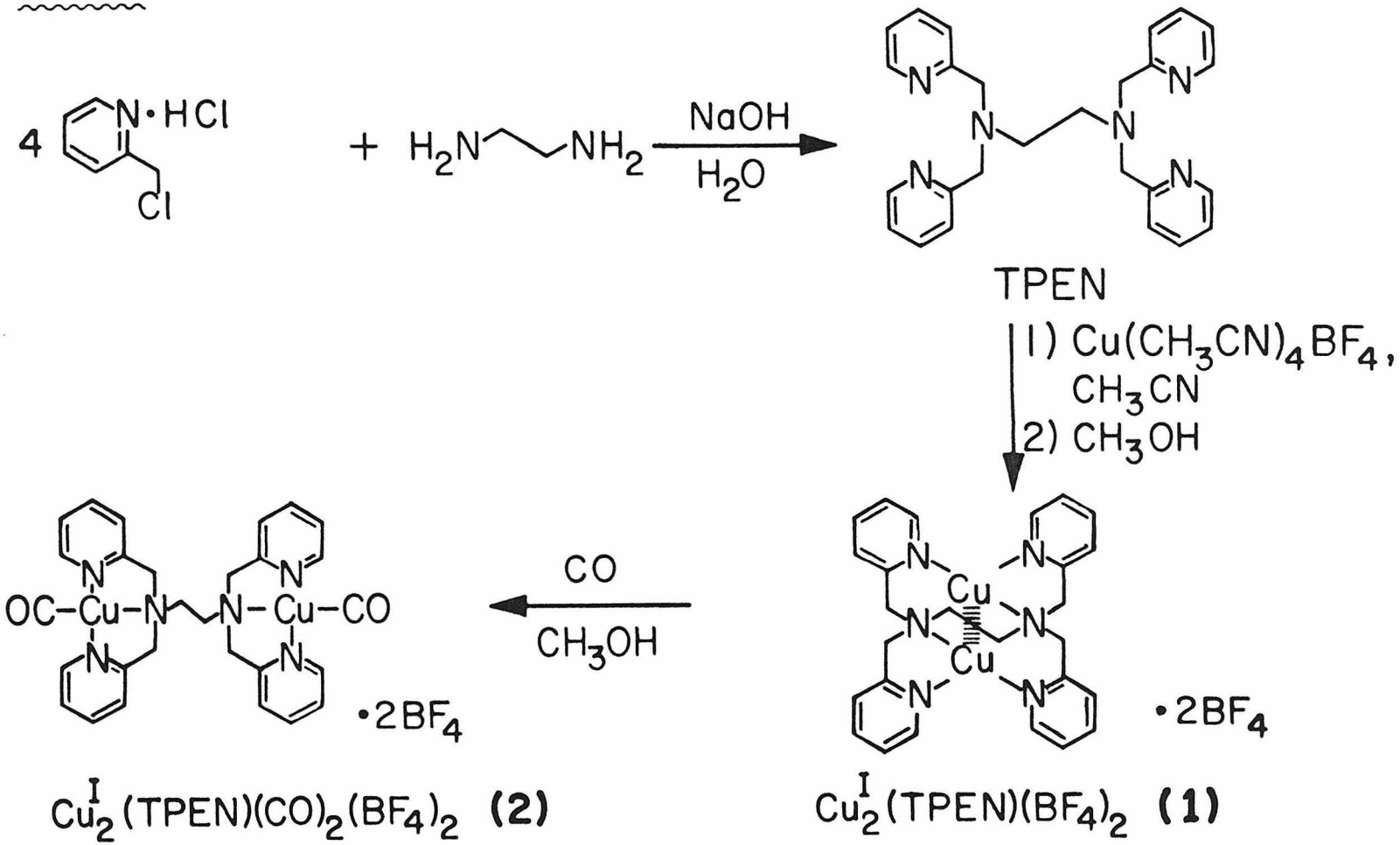
These structures show that the TPEN ligand is capable of binding a pair of cuprous ions in two distinctly different fashions. In compound 1, $Cu_2(TPEN)(BF_4)_2$, there is a significant intramolecular copper-copper interaction, with the ligand folded over on itself; but in the carbonyl adduct, 2, the copper-nitrogen bonds have undergone extensive rearrangement and there is no direct Cu-Cu interaction.

Synthesis and Characterization of Complexes

The methods used in preparing the ligand and its cuprous complexes are outlined in Scheme 1. Compound 1, $Cu_2(TPEN)(BF_4)_2$, is only slightly soluble in methanol, but saturation of a methanol suspension with carbon monoxide results in complete dissolution. Upon purging this colorless solution with nitrogen, compound 1 (identified by IR) is reprecipitated. This process is totally reversible and may be repeated at will. Evaporation of the methanol with a stream of CO gives off-white crystals of the dicarbonyl, $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2.

Shown in Figure 1 are the structures of the complex cations of compounds 1 and 2, as determined by single-crystal X-ray diffraction. In compound 1 each copper atom is bound between two pyridine rings, while forming a much weaker third bond with one of the tertiary amine nitrogens. The two pyridine rings in this case originate from different nitrogens of the ethylenediamine moiety. Significant interaction between the two copper atoms themselves is indicated by the metal-metal separation of 2.78 Å. In compound 2 an additional ligand, carbon monoxide, has moved into the inner coordination sphere of each copper, and the direct metal-metal interaction no longer occurs. Each

Scheme 1



$Cu^{I}_2(TPEN)(BF_4)_2$ **(1)**

$Cu^{I}_2(TPEN)(CO)_2(BF_4)_2$ **(2)**

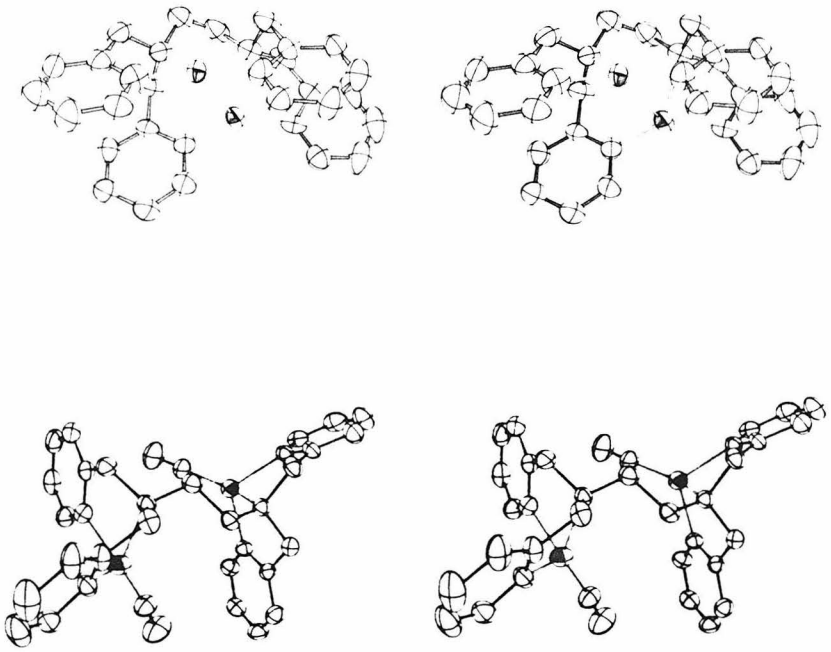
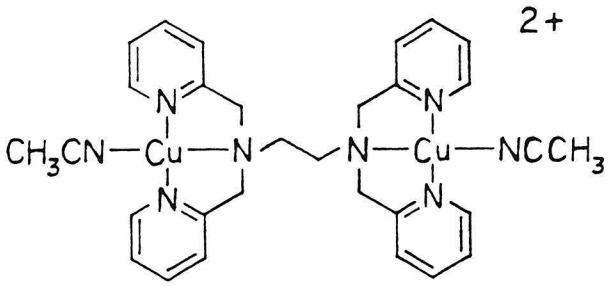


Figure 1. Stereodrawings of $Cu_2(TPEN)^{2+}$ (top) and $Cu_2(TPEN)(CO)_2^{2+}$ (bottom).

copper atom has assumed a pseudotetrahedral geometry, with the other three bound groups consisting of an amine nitrogen and the two pyridylmethyl groups attached to it. These structures are described in further detail in the following sections.

Compound 1 is pale green in appearance in the solid state, but the visible spectrum of the solid (Nujol mull, under He) shows no absorption above 450 nm. Although the compound is insoluble in most organic solvents (e. g., CH_2Cl_2, CH_3OH), it is very soluble in acetonitrile, forming a deep yellow solution. This color change upon dissolution may be indicative of coordination of CH_3CN to copper to give a structure similar to that observed for the carbonyl adduct (structure 3).



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Compound 1 also dissolves in N, N-dimethylformamide, but the solution immediately turns blue and copper metal is plated out. This disproportionation reaction can be reversed entirely by purging the solution with carbon monoxide, resulting in a colorless solution which presumably contains the carbonyl adduct, 2.

As expected, compound $\underset{\sim}{1}$ is diamagnetic and gives very sharp proton NMR signals (Figure 2). In Table I are listed the chemical shifts for both complex $\underset{\sim}{1}$ and the free ligand in CD_3CN solution. These spectra confirm the identity of the organic entity. The binding of copper(I) is evidenced in the spectrum of the complex by the rather large changes in the chemical shifts relative to the free ligand. The resonances due to the methylene protons (α and β) and to three of the pyridine protons (py_4, py_5, py_6) all move downfield upon binding of the positive metal ion.[4] The py_3 resonance, on the other hand, shows an upfield shift. This anomalous behavior could be the result of pyridine ring current effects.

The infrared spectrum of the carbonyl complex, $\underset{\sim}{2}$, has been examined in both solution and the solid state. In methylene chloride solution a single carbonyl stretching band is observed at 2110 cm^{-1}. This frequency is very high compared to those found in other copper(I) carbonyl complexes.[2,5,6] The cationic character and the "soft" pyridine ligands of $\underset{\sim}{2}$ may result in less π donation from copper(I) into the π^* orbital of CO, thereby raising the frequency of the CO stretch. The solid state IR spectrum of $\underset{\sim}{2}$ (Nujol mull) exhibits a strong, sharp pair of CO bands at 2097 and 2107 cm^{-1}, consistent with the observation of two nonequivalent carbonyl groups in the crystal structure of the compound (vide infra).

While neither $Cu_2(TPEN)(BF_4)_2$ nor its carbonyl adduct shows reactivity toward oxygen in the solid state, solutions of the latter

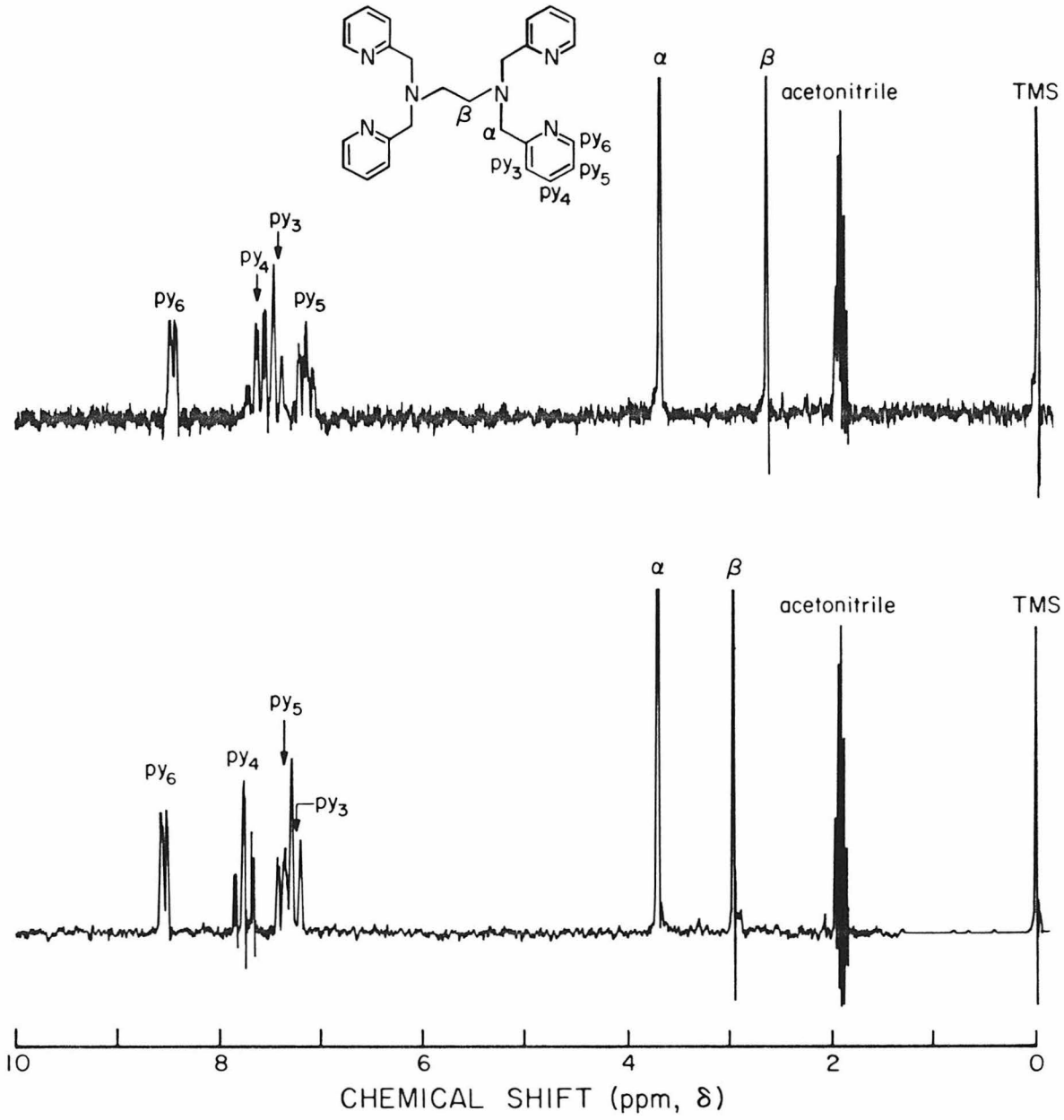


Figure 2. NMR spectra of the TPEN ligand (top) and $Cu_2(TPEN)(BF_4)_2$, 1 (bottom) in CD_3CN at 34 °C.

Table I. Proton NMR Frequencies for TPEN and $Cu_2(TPEN)(BF_4)_2$[a]

Compound	α	β	py_3	py_4	py_5	py_6
TPEN	3.68	2.63	7.39	7.62	7.11	8.44
$Cu_2(TPEN)(BF_4)_2$	3.72	2.98	7.23	7.77	7.34	8.55

[a]All spectra were obtained in CD_3CN solution at 34°C under an atmosphere of helium. The values listed are given in parts per million, δ, relative to Me_4Si. The assignments for the resonances are given in Figure 1.

(2) in CH_2Cl_2, CH_3OH, or DMF change from colorless to blue. This reaction cannot be reversed by purging the solutions with argon. The autoxidation products have not been characterized.

Crystallographic Analysis of $Cu_2(TPEN)(BF_4)_2$, 1.

Table II summarizes the basic crystal data for both compounds 1 and 2. The atomic labeling scheme for $Cu_2(TPEN)^{2+}$ is shown in Figure 3. The dication lies on a crystallographic two-fold rotation axis, and primes are used to designate symmetry-related atoms within the same complex. The atomic parameters and interatomic distances and angles are given in Tables III-VI.

The outstanding feature of the structure of the $Cu_2(TPEN)^{2+}$ cation is its extreme compactness (see Figures 1 and 3). The gauche conformation of the ethylenediamine "backbone" (N-C-C-N torsion angle = 52°) permits each cuprous ion to coordinate to pyridine groups from opposite ends of the ethylenediamine chain, and more importantly allows the close intramolecular copper-copper contact of 2.779(2) Å.

The coordination about copper (crystallographically identical for the two atoms) is difficult to place in a particular geometric category. As suggested by Figures 1 and 3, each metal ion deviates only slightly (0.07 Å) from the plane defined by the three nitrogen atoms to which it is bound, the direction of this deviation being that which gives the shorter Cu-Cu′ distance. The bonds to the two pyridine nitrogens form a large, but not linear, angle about copper of 146.8°, and the lengths of these bonds are at the low end of the range usually found for Cu^I coordinated to nitrogen (Cu-N1 = 1.94 Å, Cu-N16′ =

Table II. Crystal Data for $Cu_2(TPEN)(BF_4)_2$, 1, and $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2.

Compound	$Cu_2(TPEN)(BF_4)_2$	$Cu_2(TPEN)(CO)_2(BF_4)_2$
Formula (per asymmetric unit)	$C_{26}H_{28}B_2Cu_2F_8N_6$	$C_{28}H_{28}B_2Cu_2F_8N_6O_2$
Formula weight	725.25	781.27
Space group	C2/c (no. 15)	$P2_1/c$ (no. 14)
a, Å	13.099(4)	17.706(5)
b, Å	15.974(6)	10.372(3)
c, Å	14.472(5)	19.601(5)
β, deg	102.74(2)	112.77(2)
V, $Å^3$	2953.7(17)	3319.2(16)
Z	4	4
ρ_{calcd}, g/cm^3	1.63	1.56
μ, cm^{-1}	15.8	23.7
radiation	MoK_α	CuK_α
λ, Å	0.71069	1.5418

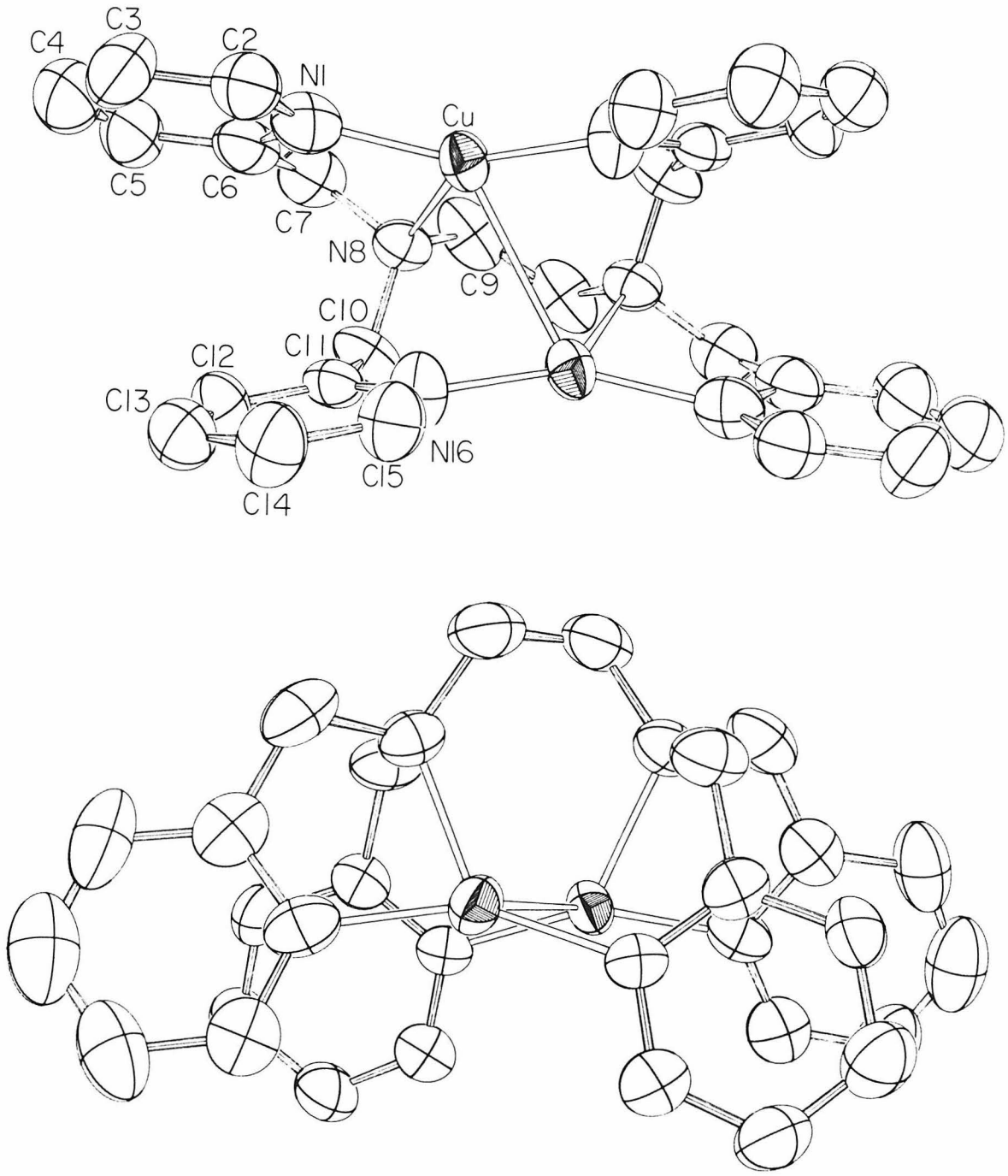


Figure 3. ORTEP drawings of $Cu_2(TPEN)^{2+}$, including the atomic labeling scheme. Ellipsoids of 40% probability are shown. The twofold axis is perpendicular to the page in the upper diagram and parallel to it in the lower.

Table III. Atomic Parameters and esd's for the Nonhydrogen Atoms of $Cu_2(TPEN)(BF_4)_2$, 1, and $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2.

	x[a]	y	z	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$Cu_2(TPEN)(BF_4)_2$									
Cu	3656(9)	3694(8)	16687(9)	470(8)	592(8)	691(9)	-81(10)	59(6)	28(11)
N1	1769(5)	191(5)	1486(5)	87(6)	62(7)	72(6)	-18(5)	10(5)	-17(5)
C2	2163(8)	-550(6)	1290(6)	83(6)	93(10)	77(8)	-3(8)	16(7)	1(7)
C3	3216(9)	-660(7)	1271(7)	95(10)	150(13)	97(10)	33(9)	46(9)	15(9)
C4	3879(8)	1(9)	1469(8)	85(9)	194(17)	99(10)	15(9)	28(8)	36(10)
C5	3508(9)	750(7)	1679(7)	67(8)	166(14)	94(10)	-23(9)	22(8)	33(9)
C6	2448(8)	839(6)	1698(6)	87(9)	90(9)	59(8)	-11(8)	6(7)	9(7)
C7	1956(8)	1664(6)	1873(7)	95(9)	81(9)	82(9)	-29(7)	15(7)	18(7)
N8	1124(5)	1554(4)	2418(5)	76(6)	58(6)	58(6)	-8(5)	8(5)	7(5)
C9	451(7)	2323(5)	2247(7)	91(10)	56(7)	121(11)	-10(6)	-18(8)	9(7)
C10	1601(7)	1426(6)	3447(6)	96(8)	57(7)	71(8)	-5(6)	-15(7)	6(7)
C11	1864(7)	525(6)	3654(5)	71(7)	64(8)	46(6)	8(7)	7(6)	10(6)
C12	2888(7)	248(6)	3909(6)	59(7)	81(8)	86(8)	-11(7)	3(6)	-2(8)
C13	3100(7)	-594(6)	4080(6)	82(8)	93(10)	88(8)	16(7)	17(7)	20(8)
C14	2245(8)	-1129(6)	4034(7)	88(9)	69(8)	119(10)	19(7)	32(8)	22(8)
C15	1246(8)	-793(6)	3802(7)	79(8)	69(8)	103(9)	6(7)	25(7)	-1(7)
N16	1045(6)	14(5)	3621(5)	67(6)	49(6)	122(8)	5(5)	26(5)	13(6)
F1A	4136(6)	2337(5)	390(6)	66(6)	90(7)	176(9)	-4(5)	20(6)	-14(6)
F2A	5526(8)	2097(8)	1446(7)	114(7)	305(13)	66(8)	1(9)	16(6)	-39(8)
F3A	5387(8)	1686(6)	-118(6)	149(9)	111(8)	102(8)	51(7)	20(6)	-35(6)
F4A	5484(10)	3076(7)	218(8)	220(12)	133(10)	186(11)	116(9)	108(9)	-37(8)

Table III. Atomic Parameters and esd's for the Nonhydrogen Atoms of $Cu_2(TPEN)(BF_4)_2$, 1, and $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2. (cont'd)

F1B	473(2)	283(2)	14(2)	13.8(1.2)[c]
F2B	587(2)	251(1)	136(2)	10.3(0.9)
F3B	522(2)	157(2)	53(2)	14.1(1.1)
F4B	627(2)	234(2)	17(2)	11.6(0.9)
BA	513(0)	230(0)	48(0)	8.5(0.7)
BB	552(0)	231(0)	55(0)	6.2(1.4)

Table III. Atomic Parameters and esd's for the Nonhydrogen Atoms of $Cu_2(TPEN)(BF_4)_2$, 1, and $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2. (cont'd)

$Cu_2(TPEN)(CO)_2(BF_4)_2$

Cu	64488(5)	12678(9)	30151(5)	569(5)	670(6)	633(6)	-7(5)	114(5)	-10(5)
Cu′	81118(5)	27758(8)	17656(5)	574(5)	604(6)	655(6)	4(5)	208(5)	-64(5)
O18	5329(3)	1361(6)	1472(3)	103(4)	138(5)	69(4)	25(4)	-13(3)	-3(4)
O18′	7923(4)	5020(6)	2558(4)	142(5)	107(5)	166(6)	14(4)	62(5)	-62(4)
B1	3857(5)	2529(10)	3087(6)	74(6)	86(8)	96(8)	16(6)	16(6)	-16(6)
B2	553(5)	2391(11)	4120(6)	56(6)	95(9)	122(9)	5(6)	-2(6)	8(8)
F1	4497(3)	2591(7)	2889(4)	128(4)	246(7)	190(6)	16(5)	92(4)	35(5)
F2	3888(3)	3461(6)	3576(3)	131(4)	178(6)	136(4)	21(4)	8(4)	-84(4)
F3	3918(3)	1372(6)	3433(3)	111(4)	139(5)	157(5)	29(3)	34(4)	43(4)
F4	3155(3)	2608(5)	2490(2)	103(3)	117(4)	101(3)	37(3)	-15(3)	-21(3)
F5	-203(4)	2925(7)	3967(6)	116(5)	140(6)	452(14)	-19(4)	25(7)	78(8)
F6	471(3)	1287(5)	4428(3)	147(4)	85(3)	142(4)	-1(3)	45(4)	15(3)
F7	1061(3)	3182(5)	4591(3)	107(4)	158(5)	158(5)	-59(4)	7(3)	-51(4)
F8A	296(8)	2600(11)	3442(5)	205(14)	148(10)	46(6)	-58(10)	13(8)	4(6)
F8B	960(8)	2029(16)	3690(7)	152(11)	336(20)	124(10)	-18(12)	97(9)	-31(12)
N1	6808(3)	3015(5)	3516(3)	63(3)	54(4)	54(3)	-1(3)	23(3)	-2(3)
N16	6321(3)	-39(5)	3734(3)	57(3)	53(4)	78(4)	-8(3)	40(3)	-8(3)
N8	7728(3)	813(5)	3639(2)	43(3)	55(3)	44(3)	-4(3)	20(3)	5(3)
N16′	9140(3)	2526(5)	1556(2)	44(3)	62(4)	46(3)	-8(3)	19(3)	1(3)
N1′	7137(3)	2159(5)	866(2)	44(3)	54(4)	45(3)	3(3)	14(3)	2(3)
N8′	8276(3)	730(4)	1979(2)	44(3)	54(3)	42(3)	3(3)	18(3)	2(3)
C17	5776(4)	1289(7)	2047(4)	66(5)	75(5)	66(5)	12(4)	9(4)	-3(5)
C6	7581(4)	3044(6)	4018(3)	59(4)	69(5)	47(4)	-7(4)	30(4)	-3(4)
C5	7967(4)	4201(7)	4325(4)	73(5)	82(6)	72(5)	-17(4)	40(4)	-22(5)
C4	7542(5)	5315(7)	4115(4)	108(7)	71(6)	96(6)	-23(5)	64(5)	-30(5)
C3	6756(5)	5299(7)	3602(4)	107(6)	63(5)	84(6)	9(5)	61(5)	6(5)
C2	6407(4)	4138(7)	3320(4)	72(5)	60(5)	73(5)	5(4)	28(4)	-5(4)
C11	7005(4)	-660(6)	4159(3)	81(5)	41(4)	66(5)	2(4)	46(4)	5(4)
C12	7049(5)	-1400(7)	4755(4)	126(7)	55(5)	97(6)	12(5)	72(5)	6(4)
C13	6346(6)	-1533(7)	4905(5)	189(10)	49(5)	141(8)	-6(6)	123(8)	7(5)

Table III. Atomic Parameters and esd's for the Nonhydrogen Atoms of $Cu_2(TPEN)(BF_4)_2$, 1, and $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2. (cont'd)

C14	5651(6)	-956(8)	4449(5)	138(8)	63(6)	170(9)	-27(5)	119(8)	-21(6)
C15	5637(4)	-208(7)	3869(4)	77(5)	62(5)	117(6)	-18(4)	54(5)	-29(5)
C7	7977(4)	1766(7)	4251(3)	53(4)	84(5)	45(4)	-11(4)	17(3)	-2(4)
C10	7719(4)	-495(6)	3935(3)	63(4)	65(5)	58(4)	11(4)	27(4)	12(4)
C9	8280(3)	914(6)	3246(3)	49(4)	71(5)	54(4)	-3(3)	17(3)	3(4)
C17′	7984(4)	4132(7)	2268(4)	72(5)	77(6)	91(6)	7(4)	26(4)	-28(5)
C11′	9486(3)	1372(6)	1741(3)	38(4)	76(5)	51(4)	2(4)	20(3)	5(4)
C12′	10103(4)	979(7)	1525(4)	64(5)	88(6)	93(6)	-1(4)	40(4)	-2(5)
C13′	10375(4)	1827(9)	1132(5)	69(5)	141(8)	113(7)	-19(5)	63(5)	-12(6)
C14′	10044(5)	3015(8)	965(4)	90(6)	104(7)	80(6)	-42(5)	41(5)	-3(5)
C15′	9423(4)	3332(6)	1186(3)	63(5)	78(5)	51(4)	-21(4)	17(4)	-1(4)
C6′	7083(3)	886(6)	780(3)	51(4)	52(4)	39(4)	-4(4)	21(3)	-1(3)
C5′	6405(4)	313(6)	262(3)	76(5)	52(5)	61(5)	-8(4)	31(4)	-5(4)
C4′	5767(4)	1070(7)	-202(3)	55(4)	86(6)	50(4)	-12(4)	8(4)	-7(4)
C3′	5825(4)	2353(7)	-122(3)	55(4)	78(5)	55(4)	7(4)	18(4)	15(4)
C2′	6518(4)	2875(6)	417(4)	61(4)	49(4)	71(5)	-3(4)	25(4)	6(4)
C10′	9167(3)	539(6)	2192(3)	49(4)	69(5)	59(4)	16(4)	20(3)	8(4)
C7′	7827(3)	129(6)	1242(3)	55(4)	50(4)	54(4)	2(3)	23(3)	-2(3)
C9′	7987(3)	166(6)	2526(3)	51(4)	61(4)	58(4)	-5(3)	26(3)	0(4)

[a]Fractional coordinates have been multiplied by 10^5 for the copper atoms and 10^4 otherwise. U_{ij} has been multiplied by 10^4 for the copper atoms and 10^3 otherwise. [b]The form of the thermal ellipsoid is $\exp[-2\pi^2 (U_{11}h^2 a^{*2} + \cdots + 2\ U_{23}klb^*c^*)]$ for the anisotropic thermal parameters. [c]Isotropic B values ($Å^2$) are given for F1B, F2B, F3B, F4B, BA, and BB.

Table IV. Hydrogen Atomic Parameters for $Cu_2(TPEN)(BF_4)_2$, 1, and $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2.[a]

	x[b]	y	z	B, Å^2
$Cu_2(TPEN)(BF_4)_2$				
H2	170	-103	116	7.8
H3	348	-120	112	7.8
H4	461	-6	146	8.2
H5	397	123	181	8.0
H7A	165	192	127	7.2
H7B	250	203	222	7.2
H9A	16	237	157	8.0
H9B	89	281	246	8.0
H10A	110	160	382	7.3
H10B	223	176	362	7.3
H12	346	64	397	6.6
H13	381	-80	423	7.4
H14	235	-172	417	6.7
H15	66	-117	377	7.1

Table IV. Hydrogen Atomic Parameters for $Cu_2(TPEN)(BF_4)_2$, 1, and $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2. (cont'd)

$Cu_2(TPEN)(CO)_2(BF_4)_2$

H2	588	414	299	6.1
H3	648	605	345	6.8
H4	778	607	431	7.0
H5	848	422	466	6.4
H7A	785	146	462	5.5
H7B	853	187	443	5.5
H9A	833	175	315	5.4
H9B	878	62	354	5.4
H10A	769	-109	359	5.6
H10B	819	-63	433	5.6
H12	753	-179	505	7.7
H13	635	-198	530	8.6
H14	519	-108	453	8.1
H15	516	17	357	7.3
H2′	655	374	47	5.8
H3′	542	286	-41	6.0
H4′	532	70	-55	6.3
H5′	638	-56	22	5.8
H7A′	817	6	100	5.2
H7B′	767	-68	131	5.2
H9A′	744	14	233	5.1
H9B′	817	-65	262	5.1
H10A′	943	72	268	5.6
H10B′	927	-30	213	5.6
H12′	1032	18	164	7.3
H13′	1077	159	98	8.4
H14′	1023	358	72	7.6
H15′	920	413	108	6.0

[a]Each atom is given the same number as the carbon to which it is bound. [b]Fractional coordinates have been multiplied by 10^3.

Table V. Interatomic Distances (Å) for $Cu_2(TPEN)(BF_4)_2$, 1, and $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2.

$Cu_2(TPEN)(BF_4)_2$[a]

Cu-Cu′	2.779(2)	C11-C12	1.383(12)
Cu-N1	1.936(7)	C11-N16	1.339(11)
Cu-N8	2.295(7)	C12-C13	1.384(13)
Cu-N16′	1.890(8)	C13-C14	1.399(14)
N1-C2	1.346(12)	C14-C15	1.386(14)
N1-C6	1.355(12)	C15-N16	1.330(12)
C2-C3	1.398(15)	BA-F1A	1.284
C3-C4	1.356(16)	BA-F2A	1.411
C4-C5	1.353(16)	BA-F3A	1.398
C5-C6	1.402(15)	BA-F4A	1.406
C6-C7	1.513(14)	BB-F1B	1.36
C7-N8	1.490(12)	BB-F2B	1.20
N8-C9	1.501(11)	BB-F3B	1.24
N8-C10	1.496(11)	BB-F4B	1.23
C9-C9′	1.521(13)	Cu-N16	2.827(8)
C10-C11	1.495(13)		

Table V. Interatomic Distances for $Cu_2(TPEN)(BF_4)_2$, 1, and $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2 (cont'd).

$Cu_2(TPEN)(CO)_2(BF_4)_2$

Cu-N1	2.042(5)	Cu'-N1'	2.036(5)
Cu-N16	2.030(5)	Cu'-N16'	2.032(5)
Cu-N8	2.169(5)	Cu'-N8'	2.160(5)
Cu-C17	1.809(7)	Cu'-C17'	1.781(7)
N1-C6	1.341(8)	N1'-C6'	1.330(8)
N1-C2	1.341(9)	N1'-C2'	1.334(9)
N16-C11	1.340(8)	N16'-C11'	1.329(8)
N16-C15	1.346(9)	N16'-C15'	1.326(8)
N8-C7	1.482(8)	N8'-C7'	1.489(8)
N8-C10	1.479(8)	N8'-C10'	1.481(8)
N8-C9	1.465(8)	N8'-C9'	1.476(8)
C17-O18	1.100(9)	C17'-O18'	1.110(10)
C6-C5	1.396(9)	C6'-C5'	1.372(9)
C6-C7	1.487(9)	C6'-C7'	1.499(9)
C5-C4	1.353(11)	C5'-C4'	1.387(9)
C4-C3	1.366(11)	C4'-C3'	1.340(10)
C3-C2	1.369(11)	C3'-C2'	1.383(10)
C11-C12	1.375(9)	C11'-C12'	1.378(9)
C11-C10	1.500(9)	C11'-C10'	1.494(8)
C12-C13	1.391(11)	C12'-C13'	1.374(11)
C13-C14	1.350(12)	C13'-C14'	1.350(11)
C14-C15	1.369(11)	C14'-C15'	1.368(10)
C9-C9'	1.515(9)	B2-F5	1.369(14)
B1-F1	1.333(13)	B2-F6	1.327(12)
B1-F2	1.347(13)	B2-F7	1.301(12)
B1-F3	1.362(13)	B2-F8A	1.247(16)
B1-F4	1.340(14)	B2-F8B	1.356(19)
Cu-Cu'	4.764(1)		

[a]For compound 1 only, primes are used to designate atoms operated upon by the twofold axis (i.e., $\bar{x}$, y, $\frac{1}{2}$ -z).

Table VI. Interatomic Angles (deg) for $Cu_2(TPEN)(BF_4)_2$, 1, and $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2.

$Cu_2(TPEN)(BF_4)_2$[a]

N1-Cu-Cu′	129.6(2)	C11-C10-N8	111.0(7)
N8-Cu-Cu′	77.7(2)	C12-C11-C10	121.9(8)
N16′-Cu-Cu′	71.7(2)	N16-C11-C10	115.5(8)
N8-Cu-N1	82.0(3)	N16-C11-C12	122.5(8)
N16′-Cu-N1	146.8(3)	C13-C12-C11	120.2(8)
N16′-Cu-N8	130.8(3)	C14-C13-C12	117.3(9)
C2-N1-Cu	125.3(6)	C15-C14-C13	118.6(9)
C6-N1-Cu	116.9(6)	N16-C15-C14	123.9(9)
C6-N1-C2	117.2(8)	C11-N16-Cu′	124.1(6)
C3-C2-N1	122.7(9)	C15-N16-Cu′	118.4(6)
C4-C3-C2	119.2(10)	C15-N16-C11	117.5(8)
C5-C4-C3	119.5(11)	F2A-BA-F1A	104.9
C6-C5-C4	120.0(10)	F3A-BA-F1A	110.0
C5-C6-N1	121.5(9)	F4A-BA-F1A	108.4
C7-C6-N1	114.9(8)	F3A-BA-F2A	111.6
C7-C6-C5	123.5(9)	F4A-BA-F2A	113.7
N8-C7-C6	112.0(8)	F4A-BA-F3A	108.1
C7-N8-Cu	97.9(5)	F2B-BB-F1B	110.9
C9-N8-Cu	114.8(5)	F3B-BB-F1B	110.8
C10-N8-Cu	113.6(5)	F4B-BB-F1B	113.2
C9-N8-C7	106.7(7)	F3B-BB-F2B	109.1
C10-N8-C7	110.5(7)	F4B-BB-F2B	105.0
C10-N8-C9	112.1(6)	F4B-BB-F3B	107.6
C9′-C9-N8	114.3(7)		

Table VI. Interatomic Angles (deg) for $Cu_2(TPEN)(BF_4)_2$, 1, and $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2 (cont'd).

$Cu_2(TPEN)(CO)_2(BF_4)_2$

N16-Cu-N1	110.9(4)	N16′-Cu′-N1′	108.1(4)
N8-Cu-N1	81.9(4)	N8′-Cu′-N1′	82.2(4)
C17-Cu-N1	116.7(4)	C17′-Cu′-N1′	118.7(4)
N8-Cu-N16	80.6(4)	N8′-Cu′-N16′	81.4(4)
C17-Cu-N16	122.1(4)	C17′-Cu′-N16′	121.8(4)
C17-Cu-N8	135.6(4)	C17′-Cu′-N8′	134.9(4)
C6-N1-Cu	114.4(5)	C6′-N1′-Cu′	114.6(5)
C2-N1-Cu	126.9(5)	C2′-N1′-Cu′	126.9(5)
C2-N1-C6	117.9(6)	C2′-N1′-C6	114.4(5)
C11-N16-Cu	115.8(5)	C11′-N16′-Cu′	126.0(5)
C15-N16-Cu	125.0(5)	C15′-C16′-Cu′	126.0(5)
C15-N16-C11	118.7(6)	C15′-C16′-C11′	119.1(6)
C7-N8-Cu	103.3(5)	C7′-N8′-Cu′	104.0(5)
C10-N8-Cu	104.7(5)	C10′-N8′-Cu′	103.6(5)
C9-N8-Cu	116.8(5)	C9′-N8′-Cu′	118.1(5)
C10-N8-C7	109.9(6)	C10′-N8′-C7′	109.3(6)
C9-N8-C7	109.1(6)	C9′-N8′-C7′	109.5(6)
C9-N8-C10	112.5(6)	C9′-N8′-C10′	111.9(6)
O18-C17-Cu	174.7(6)	O18′-C17′-Cu′	176.0(6)
C5-C6-N1	121.7(6)	C5′-C6′-N1′	121.6(6)
C7-C6-N1	115.6(6)	C7′-C6′-N1′	116.1(6)
C7-C6-C5	122.7(6)	C7′-C6′-C5′	122.2(6)
C6-C5-C4	118.8(7)	C6′-C5′-C4′	119.8(6)
C3-C4-C5	120.1(8)	C3′-C4′-C5′	118.7(7)
C2-C3-C4	118.7(8)	C2′-C3′-C4′	118.9(7)
C3-C2-N1	122.8(7)	C3′-C2′-N1′	123.1(7)
C12-C11-N16	122.5(6)	C12′-C11′-N16′	121.3(6)
C10-C11-N16	115.1(6)	C10′-C11′-N16′	116.3(6)
C10-C11-C12	122.4(6)	C10′-C11′-C12′	122.4(6)
C13-C12-C11	118.3(7)	C13′-C12′-C11′	118.3(7)
C14-C13-C12	118.5(8)	C14′-C13′-C12′	120.5(8)
C15-C14-C13	121.3(8)	C15′-C14′-C13′	118.0(7)
C14-C15-N16	120.6(7)	C14′-C15′-N16′	122.8(6)
C6-C7-N8	112.9(6)	C6′-C7′-N8′	112.4(6)
C11-C10-N8	110.9(6)	C11′-C10′-N8′	111.1(6)
C9′-C9-N8	113.4(6)	C9-C9′-N8′	112.6(6)
F2-B1-F1	111.5(9)	F6-B2-F5	100.4(9)
F3-B1-F1	105.9(9)	F7-B2-F5	104.4(9)
F4-B1-F1	110.5(9)	F8A-B2-F5	77.0(11)
F3-B1-F2	107.7(9)	F8B-B2-F5	133.2(12)

Table VI. Interatomic Angles (deg) for $Cu_2(TPEN)(BF_4)_2$, 1, and $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2 (cont'd)

F4-B1-F1	110.3(9)	F8B-B2-F6	102.7(11)
F4-B1-F3	110.9(9)	F8A-B2-F7	121.0(10)
F7-B2-F6	112.8(10)	F8B-B2-F7	103.2(11)
F8A-B2-F6	125.1(10)	F8B-B2-F8A	56.5(12)

[a]See footnote a for Table V.

1.89 Å).[2,3,5,6] The third metal-nitrogen bond (Cu-N8) is much longer than the other two, at 2.30 Å, and must be considerably weaker. The angles about copper associated with these interactions are given in Table VI.

There are several factors that may contribute to the skewing of complex 1, i.e., the twisting of the ethylenediamine chain and canting of the Cu-Cu′ axis. The observed conformation of the TPEN ligand does aim the lone electron pair of the amine nitrogen N8 in the direction of Cu: angles at N8 are Cu-N8-C7 = 97.9°, Cu-N8-C9 = 114.8°, and Cu-N8-C10 = 113.6°. Steric factors may also be important. Of course, the skewing of the ligand does avoid total eclipsing of the pyridine rings (see bottom of Figure 3). The gauche conformation about the C9-C9′ bond is expected from basic steric considerations, and space-filling models suggest it is also necessary to allow the pyridine rings to move far enough apart to accommodate the copper atoms. The observed conformation about the N8-C9 bond (and the equivalent N8′-C9′ bond) not only allows the nitrogen lone pairs to point toward copper atoms, but also relieves van der Waals repulsions among hydrogen atoms (e.g., among H7A, H9A, and H10A′, all of which would point upward in the upper drawing of Figure 3).

The BF_4^- counterions of compound 1 have been represented as disordered between two discrete positions, although the separation between some pairs of partial atoms is sufficiently small that representation as a single anisotropic atom would probably have been as

satisfactory. In the model used, each BF_4^- group occupies two positions which differ primarily by rotation of the group with a small degree (ca. 0.5 Å) of translation. The populations of these sites are approximately 0.71 and 0.29. No fluorine atom lies within 3.5 Å of a copper atom.

Crystallographic Analysis of $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2.

A drawing of the $Cu_2(TPEN)(CO)_2^{2+}$ cation, along with the numbering scheme to be used, is shown in Figure 4. Bond lengths and angles are listed in Tables V and VI. Although the complex contains two copper ions in effectively identical chemical environments, in this case the two are not related by crystallographic symmetry. Indeed, there are some tantalizing differences between the geometries of the two halves of the complex that will be discussed later.

The ethylenediamine group of the TPEN ligand is more extended than in compound 1, with a torsion angle N-C-C-N of 152°. The copper atoms, which are connected to one another only by the ethylenediamine bridge, are far apart. The four copper-pyridine nitrogen bonds are of statistically equivalent length, averaging 2.035(3) Å. This distance is considerably greater than for the corresponding bonds in compound 1. The copper-amine nitrogen bonds, on the other hand, are considerably shorter than in 1, although the average length of 2.164(4) Å is still rather long. Thus, the geometry about copper in 2 is distorted from tetrahedral but is much more symmetric than in 1. The structures of both compounds suggest that the cuprous ion has a lower affinity for the "hard" tertiary amine nitrogen than for pyridine.

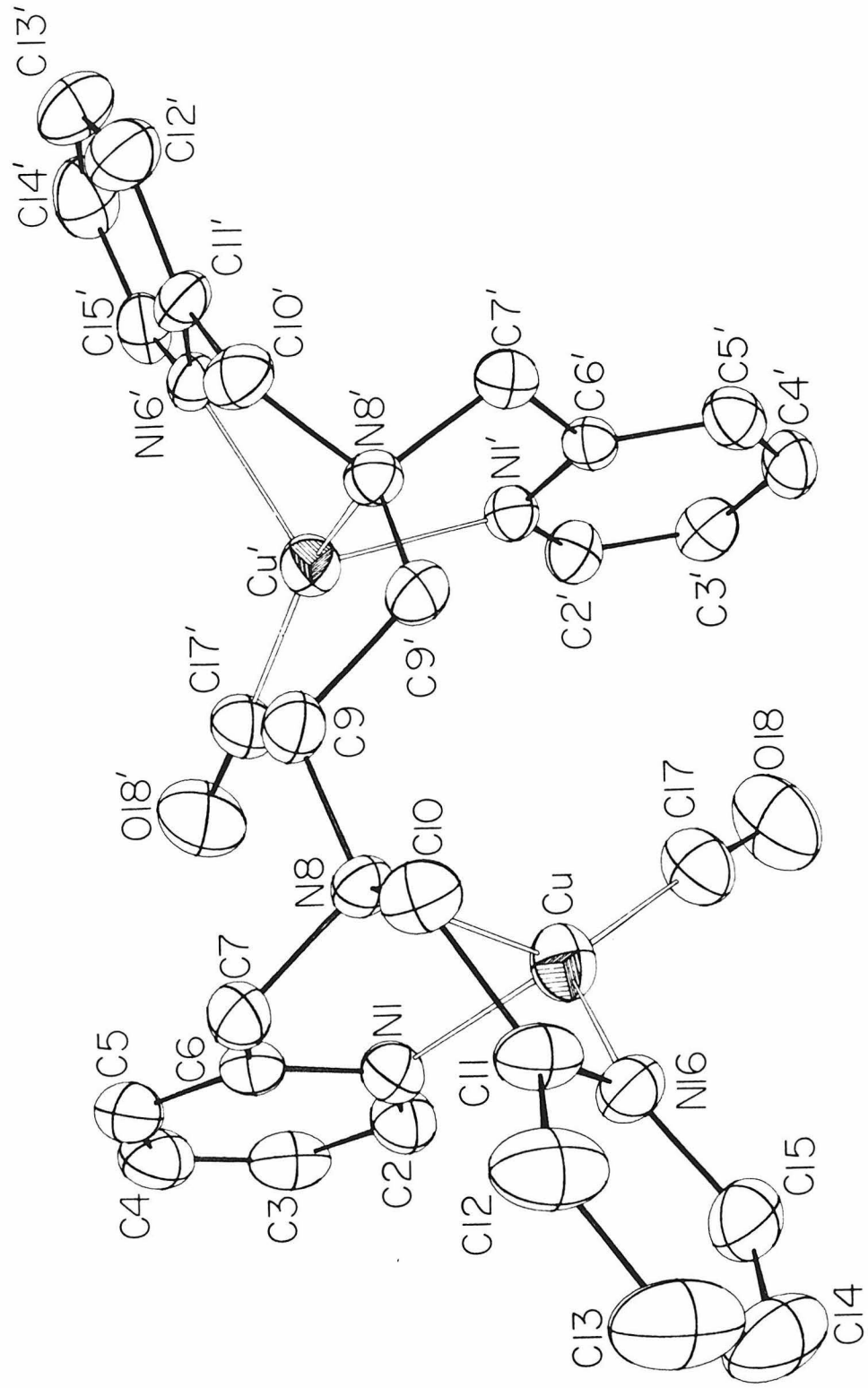


Figure 4. ORTEP drawing of $Cu_2(TPEN)(CO)_2^{2+}$, including the atomic labeling scheme. Although primes are used here, this molecule does not contain a twofold rotation axis.

The geometries of the CO ligands are especially interesting. While the C-O distances, at 1.10(1) and 1.11(1) Å, are statistically equivalent, the Cu-C distances, 1.809(7) and 1.781(7) Å, differ by nearly three esd's. This difference would not be particularly noteworthy except for the observation of two distinct CO bands in the solid-state IR spectrum. The difference between the two frequencies of 10 cm^{-1} would be expected to correspond to a difference in C-O bond lengths of less than 0.01 Å, which is within our experimental error; but the implied change in electron distribution could well result in a much larger difference in the lengths of the Cu-C bonds, as observed. Hence, there appears to be a real difference between the bonding characteristics of CO in the two halves of the complex.

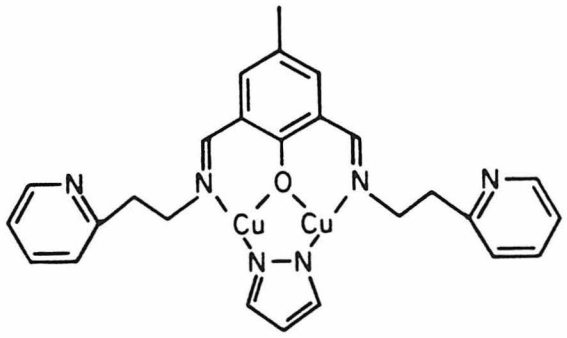
In seeking further insight into this difference, we note that the C17′-O18′ ligand nestles appreciably closer to a neighboring pyridine ring (N1-C6) than does C17-O18: the shortest interatomic distance, O18′···C4, at 3.38 Å, is nearly 0.3 Å shorter than O18···C4′, 3.66 Å; and the distance from O18′ to the center of the pyridine ring, 3.34 Å, compares with the value 3.53 Å for O18. Thus, the shorter O···pyridine contact corresponds to the shorter Cu-C bond and to the marginally longer C-O bond. Just possibly there are sufficient electronic interactions between O18′ and the pyridine ring to be reflected in a slight perturbation to the C-O and Cu-C bonds; we see no other reason for the apparent asymmetry, as there are no unusual intermolecular contacts.[7]

Of the two tetrafluoroborate anions of compound 2, one is disordered and the other is ordered, although with significant anisotropic motions of the fluorine atoms. In the former group four of the atoms (B2, F5, F6, F7) are distributed over positions sufficiently close (0.5 Å or less) that anisotropic temperature factors are adequate to describe their electron distributions. The remaining fluorine atom has a 50% occupancy of each of two positions (F8A and F8B) which are separated by about 1.2 Å.

Discussion

The apparent preference of cuprous ions for lower coordination numbers (i. e., two, three and four)[1, 3] suggested the possibility of the hexadentate TPEN performing as a bridging ligand between two coppers. The structure of the binuclear complex that was isolated was somewhat surprising, however. It had been thought that each metal might bind to an amine nitrogen and the two pyridylmethyl groups attached to it, possibly with the BF_4^- groups acting as fourth ligands. Instead, the pyridine rings that are bound to each copper originate from different nitrogens of the ethylenediamine group. There are bonds with the amine nitrogens as well, but these are quite long. The observed structure does not facilitate this copper-amine interaction, compared to other conceivable structures, whereas it does facilitate the copper-copper interaction. In fact, the peculiar conformation of the ligand and the surprisingly asymmetric bonding about the copper atoms seem to reflect a determination of the complex to form a Cu-Cu bond despite severe steric handicaps.

The coordination about copper observed for $Cu_2(TPEN)(BF_4)_2$, 1, bears some similarity to that which we recently reported for compound 4, formed with another multidentate ligand.[3] Both



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structures indicate a preference of copper(I) toward a somewhat linear arrangement of two nitrogen ligands.[9,12] This was manifested in $\underset{\wedge}{4}$ by the short Cu-N distances (all close to 1.89 Å), the rather long Cu-O distances (both about 2.09 Å), and the large N-Cu-N angles (both close to 169°). Note, however, that in both cases the third ligand (amine nitrogen or phenolate oxygen) is rather "hard" and thus unfavorable for copper(I). Therefore, the partial two-coordinate character of these compounds may simply be an avoidance of undesirable ligands. It should also be noted that systems $\underset{\wedge}{1}$ and $\underset{\wedge}{4}$ both foster a direct Cu-Cu interaction.[9,13] (In the case of compound $\underset{\wedge}{4}$ this interaction is intermolecular in the solid state. The molecules stack to give a Cu-Cu separation of 2.97 Å, compared with an intramolecular separation of 3.30 Å.)

In the presence of carbon monoxide, compound $\underset{\wedge}{1}$ undergoes extensive ligand rearrangement to form the dicarbonyl, $\underset{\wedge}{2}$. The crystal structure of $\underset{\wedge}{2}$ exhibits the "expected" pseudotetrahedral geometry with all three nitrogen ligands for each copper coming from the same end of the ethylenediamine bridge. Thus, in the TPEN system the preferred coordination about copper depends on the presence or absence of a potential fourth ligand (CO or CH_3CN). In contrast, compound $\underset{\wedge}{4}$ showed no tendency to bind CO or pyridine. Judging from molecular models, the reason for this difference is not that compound $\underset{\wedge}{4}$ cannot form a pseudotetrahedral geometry with a fourth ligand bound to copper. Evidently there is a special stabilization of cuprous ions in $\underset{\wedge}{4}$ that would be lost on binding another ligand.[12]

The origin of this stability remains unclear, however.

The structures reported in this paper, as well as those of other cuprous systems,[1-3] demonstrate that a wide variety of coordination environments can be assumed by copper(I) ions. Obviously the number and geometry of ligands preferred by copper(I) are extremely sensitive to minor ligand alterations. These effects have not been well defined, and as a result one must exercise caution in the prediction of structures for such systems.

Experimental Section

Materials. All chemicals were reagent grade and were used as received unless otherwise noted. N, N, N′, N′-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) was prepared by a modification of the literature method.[14] Tetra(acetonitrile)copper(I) tetrafluoroborate was also prepared by the published procedure.[15]

$Cu_2(TPEN)(BF_4)_2$, 1. The following was performed under helium in a Vacuum Atmospheres Dri-Lab inert atmosphere chamber. $Cu(CH_3CN)_4BF_4$ (0.315 g, 1 mmole) was added to a solution of TPEN (0.21 g, 0.5 mmole) in 25 ml of acetonitrile. After stirring for 10 min at ambient temperature, the solvent was removed under vacuum. Addition of methanol (25 ml) to the resulting orange oil yielded slightly yellow-green crystalline product. The product was collected by vacuum filtration, washed with methanol, and dried for several hours in vacuo. Anal. ($C_{26}H_{28}N_6Cu_2B_2F_8$) C, H, N.[16]

$Cu_2(TPEN)(CO)_2(BF_4)_2$, 2. A suspension of 1 (ca. 100 mg) in 20 ml of methanol (under helium) was placed in an Erlenmeyer flask and covered with a rubber septum. Purging the system with CO caused dissolution of the solid. Evaporation of the solvent with a slow stream of CO yielded off-white crystals of 2. Anal. ($C_{28}H_{28}N_6O_2Cu_2B_2F_8$) C, H, N; Cu: calcd, 16.3; found, 16.8.

Physical Measurements. Sample preparation for physical studies on the air-sensitive materials was accomplished in a Vacuum Atmospheres Dri-Lab inert atmosphere chamber, under a helium

atmosphere. Helium saturated spectroquality solvents were used for solution studies.

Electronic spectra were recorded on a Cary 14 spectrophotometer. Solid state spectra were obtained from Nujol mulls on filter paper (under He) against a Nujol-saturated filter paper as a blank.

Infrared spectra were recorded on a Beckman IR-12 Infrared Spectrophotometer. Solid state spectra were obtained from Nujol mulls pressed between KBr plates. Solution spectra were obtained using calcium fluoride solution cells (path length of 1 mm).

Proton magnetic resonance spectra were recorded on a Varian EM390 spectrophotometer at 90 MHz (34°C). The solvent utilized was CD_3CN containing TMS as the reference.

Elemental analyses were performed by the Caltech Microanalytical Laboratory.

Crystallographic Characterization of $Cu_2(TPEN)(BF_4)_2$, 1. Yellow needles were grown by slow evaporation under helium of a solution of 1 in acetonitrile/bis(2-methoxyethyl)ether (ca. 1:1). Preliminary Weissenberg and precession photographs showed the crystals to be monoclinic with the c axis parallel to the needle axis. Systematic absence of the reflections hkl with h+k odd and h0l with l odd indicated the space group to be Cc (no. 9) or C2/c (no. 15); the latter was shown to be correct by satisfactory solution and refinement of the structure.

A crystal of dimensions 0.31 mm × 0.12 mm × 0.07 mm was cut from a longer needle and mounted on a Syntex $P2_1$ four-circle diffractometer equipped with graphite-monochromatized MoK_α radiation. Cell parameters (Table II) were determined by a least-squares fit to 15 automatically centered reflections with $18° < 2\theta < 25°$. Intensity data were collected for the hemisphere ± h, ±k, l (excluding reflections with h+k odd) using $\theta - 2\theta$ scans. The maximum 2θ value was 45° for the quadrant with $k \geq 0$ and 25° for $k \leq 0$. The scan range extended from 1° below the MoK_{α_1} 2θ value to 1° above the MoK_{α_2} value, and the scan rate was 1°/min., with the total background counting time equal to the total scan time. Three check reflections were measured after every 60 reflections to monitor the crystal and instrument stability. These showed no systematic variations throughout the course of data collection.

The data were corrected for Lorentz and polarization effects and for absorption by the method of Gaussian quadrature.[17] Standard deviations of intensities were calculated using the formula

$$\sigma^2(F_o^2) = [S + (B1 + B2) + (dS)^2]/(Lp)^2$$

where S, B1, and B2 are the scan and two background counts and d was taken as 0.02.[18] After symmetry-extinct reflections were deleted, data from the two quadrants were averaged. There resulted 1941 unique data, with 1598 of these greater than zero.

With the exception of C. K. Johnson's ORTEP program, all computer programs were from the CRYM system. All scattering factors (Cu^+, F, N, C, B) with the exception of those for hydrogen[19]

were taken from the International Tables,[20] as was the real part of the anomalous dispersion correction for copper. The function minimized in the least-squares refinement was $\Sigma w(F_o^2 - F_c^2)^2$, where the weight $w = 1/\sigma^2(F_o^2)$.

The position of the copper atom was determined by means of a three-dimensional Patterson synthesis, and a subsequent electron density map revealed the positions of most of the carbon and nitrogen atoms. A cycle of least-squares, followed by another Fourier map, gave the positions of the remaining nonhydrogen atoms. Full matrix least-squares refinement including all of these atoms with isotropic temperature factors led to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.111$ for those reflections with $F_o^2 > 3\sigma$. Use of anisotropic temperature factors lowered R to 0.067. Hydrogen atom positions were calculated assuming a carbon-hydrogen distance of 0.97 Å. All of these corresponded to regions of positive electron density in a difference Fourier map. Hydrogen atoms were included in the least-squares with the isotropic temperature factor for each fixed at 1.0 $Å^2$ greater than that previously determined for the bound carbon atom. The hydrogen positional parameters were not refined but were recalculated periodically.

The large and highly anisotropic temperature factors which had been determined at this point for the fluorine and boron atoms indicated a probability of disordering of the BF_4^- anion. A detailed Fourier map of the anion showed that the fluorine atoms occupied

two different sets of positions, although one of these sets had a much lower occupancy than the other. Consequently, two partial BF_4^- groups were included in the least-squares along with a single population factor. The fluorine atoms in the more and less heavily occupied positions were refined with anisotropic and isotropic temperature factors, respectively. The boron atom for each of these BF_4^- groups was placed at coordinates calculated by averaging the corresponding fluorine coordinates. These coordinates were not refined but were recalculated periodically (final boron-boron separation = 0.50 Å). The isotropic temperature factors for the boron atoms were refined. The populations for the groups refined to final values of 0.71 and 0.29.

The final refinement of the structure was done by block-diagonal least-squares with two matrices. All nonhydrogen positional parameters were included in one matrix; the second contained all nonhydrogen thermal parameters, the BF_4^- population factor, and the scale factor. No reflections were omitted from this refinement. The final R was 0.051 for the 665 reflections with $F_o^2 > 3\sigma$, and 0.143 for all data. The goodness of fit, $[\Sigma w(F_o^2 - F_c^2)^2/(m-s)]^{\frac{1}{2}}$ was 1.19, where m = 1941 is the number of observations and s = 209 is the number of parameters. Features on a final difference map were between -1.4 e/Å^3 (at the position of Cu) and 1.2 e/Å^3 (near F4A). Final atomic parameters are given in Tables III and IV.

Crystallographic Characterization of $Cu_2(TPEN)(CO)_2(BF_4)_2$, 2. An approximately cubic crystal, 0.2 mm on an edge, was sealed in epoxy to prevent decomposition and was used for all X-ray diffraction measurements. Preliminary oscillation and Weissenberg photographs showed Laue symmetry 2/m with systematic absences h01 with l odd and 0k0 with k odd, indicating the monoclinic space group $P2_1/c$; the crystal was then transferred to a Syntex $P2_1$ diffractometer operating with Ni-filtered CuK_α radiation. Unit-cell dimensions were obtained by centering 15 well-scattered reflections with 2θ values ranging from 23° to 48°. Intensities were measured using a θ-2θ scan at a rate of 2°/minute with an equal amount of time spent on backgrounds; three check reflections, monitored every 100 measurements, showed no intensity decay nor abnormal fluctuations. All reflections out to $2\theta = 100°$ were measured in two different quadrants (± h,k, l and ± h, -k, -l) and were averaged to yield 3558 net intensities, of which 2998 were greater than zero.

The initial attempt at solving the structure was by manual application of direct methods based on 95 reflections with $|E|$ greater than 1.85, three origin-fixing signs and two symbolic signs. The resulting E map was not structurally reasonable because, as it turned out, one of the early sign entries was reversed. A three-dimensional Patterson map was then calculated, and quickly led to the positions of the Cu atoms. The C, N, O, B and F atoms were recovered from F_o and difference maps; the positions of the hydrogen atoms were cal-

culated using a C–H bond length of 0.9 Å. In the least-squares refinement the same quantity was minimized as in the preceding structure, with weights calculated in the same manner.

A late difference map indicated rather severe disorder for one of the BF_4^- groups: while three of the fluorine atoms could be adequately represented by large, anisotropic B's, the fourth could not and accordingly was split into two half-occupied sites separated by about 1.2 Å.

In the final least-squares cycles, three matrices were collected, each of order between 140 and 150: the coordinates of the 49 nonhydrogen atoms in one, anisotropic B's for one-half the cation and one of the BF_4^- groups in a second, and anisotropic B's of the remaining atoms, a scale factor, and an extinction parameter in the third. The final value of the goodness-of-fit was 1.87 for the 3558 measured reflections; the R factors were 0.062 for the 2998 reflections with net intensity greater than zero and 0.042 for the 2271 reflections with intensities greater than 3 esd's above background. Features on a difference map were between -0.8 and 0.6 e/Å^3, in generally uninteresting places.

All calculations were carried out on the CRYM system of programs. Final atomic parameters are given in Tables III and IV, based on the numbering scheme shown in Figure 4.

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are two CO bands (ν_{CO} = 2055, 2066 cm^{-1}).[8] The crystal structure of [hydrotris(1-pyrazolyl)borato] copper(I) carbonyl contains two nonequivalent molecules, but only one CO band is observed (ν_{CO} = 2083 cm^{-1}).[6]

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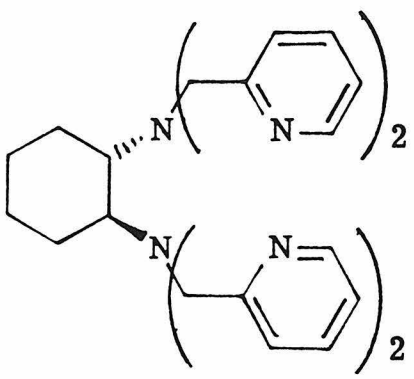
CHAPTER 3

Synthesis and Characterization of Binuclear Copper(I) Complexes of N,N,N′,N′-Tetrakis(2-pyridylmethyl)-trans-1,2-cyclohexanediamine and N,N,N′,N′-Tetrakis-(2-benzimidazolylmethyl)-trans-1,2-cyclohexanediamine

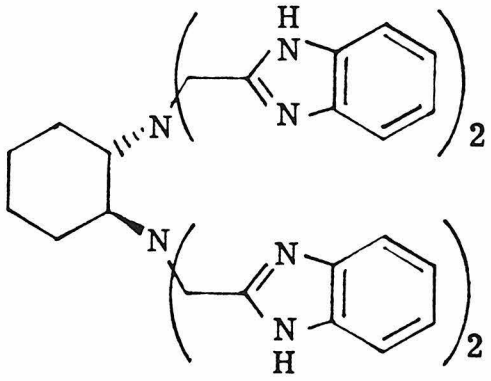
Introduction

The reaction of $Cu_2(TPEN)^{2+}$ with carbon monoxide, discussed in the preceding chapter, possesses certain features which are attractive for mimicking the addition reactions of protein binuclear copper centers. In analogy with the behavior proposed for the hemocyanin active site, $Cu_2(TPEN)^{2+}$ exhibits two different modes of coordination, depending on the presence or absence of additional ligands. Rearrangement of the solid-state structure of $Cu_2(TPEN)^{2+}$ provides a favorable pseudotetrahedral geometry with a fourth coordination site on each metal for the formation of adducts. However, because of the flexibility of the TPEN ligand, these sites are free to move to rather large distances from one another. Furthermore, in the absence of additional ligands, $Cu_2(TPEN)^{2+}$ lacks stability in solution. The complexes described in this chapter have been synthesized in order to examine the possibility that a more constrained ligand might stabilize the native complex as well as adducts with small molecules bridged between the metals. Bridging ligation of dioxygen appears to be important in the formation of stable adducts in copper-containing biological systems (see Chapter 1). One of the ligands to be presented, denoted as

CHXNpy, is an analogue of TPEN in which the ethylenediamine moiety has been replaced by the more rigid trans-1,2-cyclohexanediamine. A second ligand, CHXNbim, contains benzimidazole rather than pyridine groups. The former heterocycles bear greater resemblance than pyridine to the imidazoles of biological systems.



CHXNpy



CHXNbim

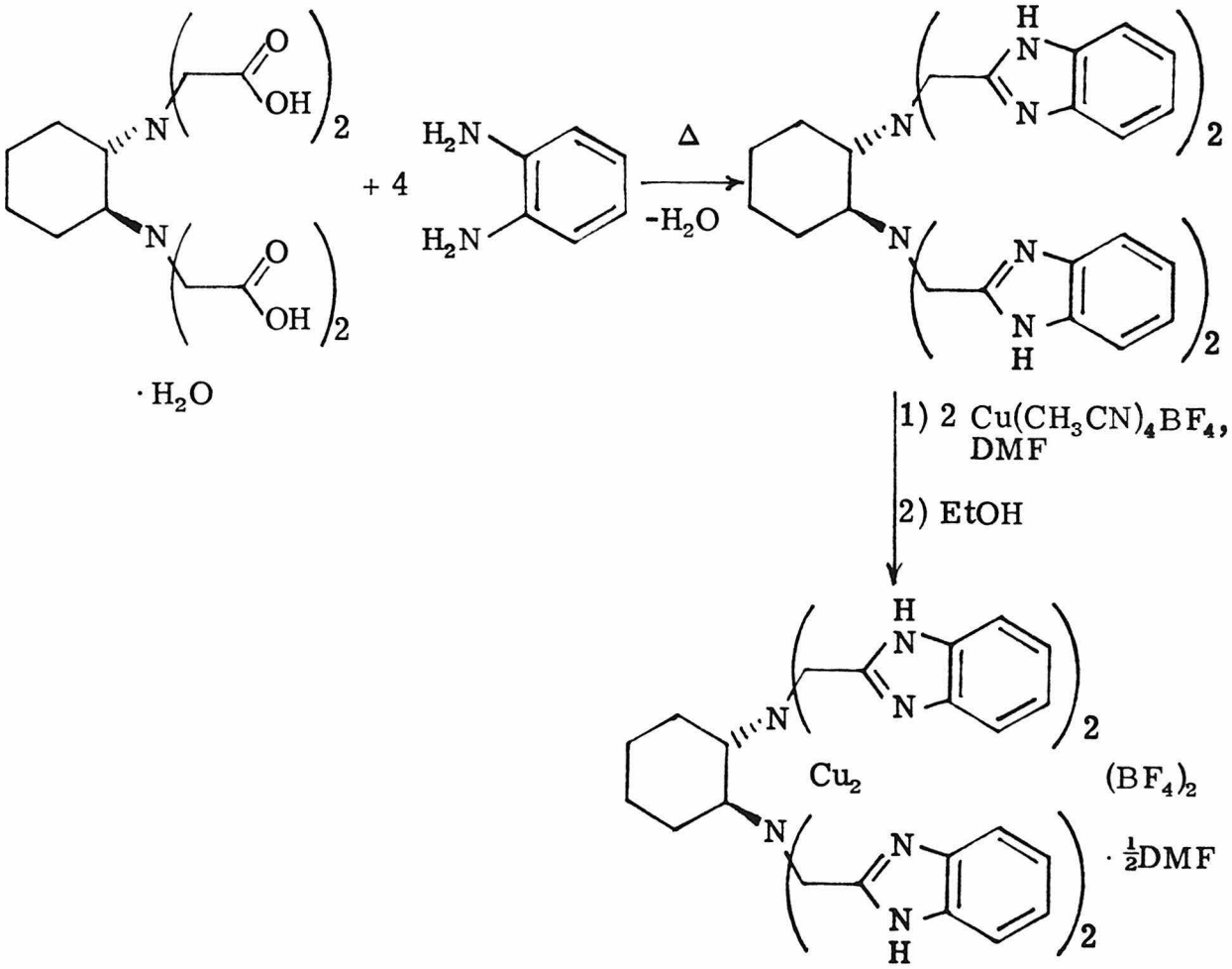
Synthesis of $Cu_2(CHXNpy)(BF_4)_2$ and $Cu_2(CHXNbim)(BF_4)_2 \cdot \frac{1}{2}DMF$

The compound $Cu_2(CHXNpy)(BF_4)_2$ was prepared by a procedure analogous to that used for $Cu_2(TPEN)(BF_4)_2$ (see Scheme 1 of Chapter 2). Reaction of picolyl chloride with racemic trans-1,2-cyclohexanediamine in aqueous base gave the ligand as a pale yellow oil after purification by chromatography. Combination of this with $Cu(CH_3CN)_4BF_4$ produced the complex, which was isolated as a yellow-green microcrystalline solid, similar in appearance to $Cu_2(TPEN)(BF_4)_2$.

The benzimidazole ligand was prepared by a method similar to various literature procedures.[1] The ligand was isolated as a white

microcrystalline solid from the material obtained by heating an intimate mixture of o-phenylenediamine and racemic trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (Scheme 1).

Scheme 1



The complex was obtained as a white microcrystalline solid after treatment of the ligand with $Cu(CH_3CN)_4BF_4$ in N,N-dimethylformamide (DMF).

Unfortunately, like $Cu_2(TPEN)(BF_4)_2$, $Cu_2(CHXNpy)(BF_4)_2$ disproportionates in most solvents, with the exception of acetonitrile. The disproportionation of the latter compound is not always immediate, however. Dilute (millimolar) solutions of the compound in DMF, which are green, generally remain free of evidence of disproportionation (i.e., deposition of copper metal and a blue coloration) for several minutes at room temperature. Concentrated solutions disproportionate rapidly. The solubility of the compound in most other solvents (e.g., methanol, acetone, dichloromethane) is rather limited, but in some cases dilute solutions can be obtained which are stable for short periods of time at low temperatures. $Cu_2(CHXNpy)(BF_4)_2$ is very soluble in acetonitrile and, like $Cu_2(TPEN)(BF_4)_2$, its solutions in this solvent are deep yellow in color. Disproportionation of the complex in other solvents may generally be reversed by the addition of sufficient acetonitrile. This high stability and the color change upon dissolution of the solid probably result from binding of acetonitrile to the complex.

The behavior of $Cu_2(CHXNbim)(BF_4)_2$ in solution is markedly different. This compound is very soluble in dimethylsulfoxide (DMSO) and DMF, but much less soluble in acetonitrile. In all cases colorless solutions result which show no signs of disproportionation, even when heated.

The solid-state infrared spectrum of $Cu_2(CHXNpy)(BF_4)_2$ (Nujol mull, prepared under He) is similar to that of $Cu_2(TPEN)(BF_4)_2$. The

absorptions due to the tetrafluoroborate anions are not split, indicating that these are not bound to copper. It appears that the ν_3 absorption at $\sim 1050\ cm^{-1}$ of the anions in $Cu_2(CHXNbim)(BF_4)_2$ is broadened somewhat. However, this may well be a result of hydrogen bonding to the imidazole ring protons of the ligand.[2]

Proton NMR Spectra

The identities of the ligands are confirmed by their nuclear magnetic resonance spectra, shown in Figure 1. These spectra are complicated somewhat by the chirality of the cyclohexanediamine moiety. In CHXNpy the two aliphatic hydrogens of each pyridylmethyl substituent (α_1 and α_2 in Figure 1) are clearly inequivalent, as indicated by the appearance of a second-order, AB pattern ($J/\Delta\nu = 1.3$). The corresponding hydrogens in CHXNbim produce a single resonance, but it is rather broad. The diastereotopic nature of these methylene protons is a consequence of the prochirality of the methylene carbons and the chirality of the cyclohexanediamine group. It is not dependent on slow rotation. In fact, the appearance of a single set of pyridine resonances in the spectrum of CHXNpy indicates that all four pyridylmethyl groups are equivalent, which requires rapid inversion of the tertiary amine nitrogens and rotation of the carbon-nitrogen bonds.

The effect of coordination of the ligands to copper(I) is dramatic. The 90 MHz spectra recorded at ambient temperatures show greatly broadened absorptions and features not present in the spectra of the uncomplexed ligands. The most reasonable explanation for this is that bonding to copper slows the interchange of the two heterocycles attached to each amine nitrogen.[3] In the complexes this

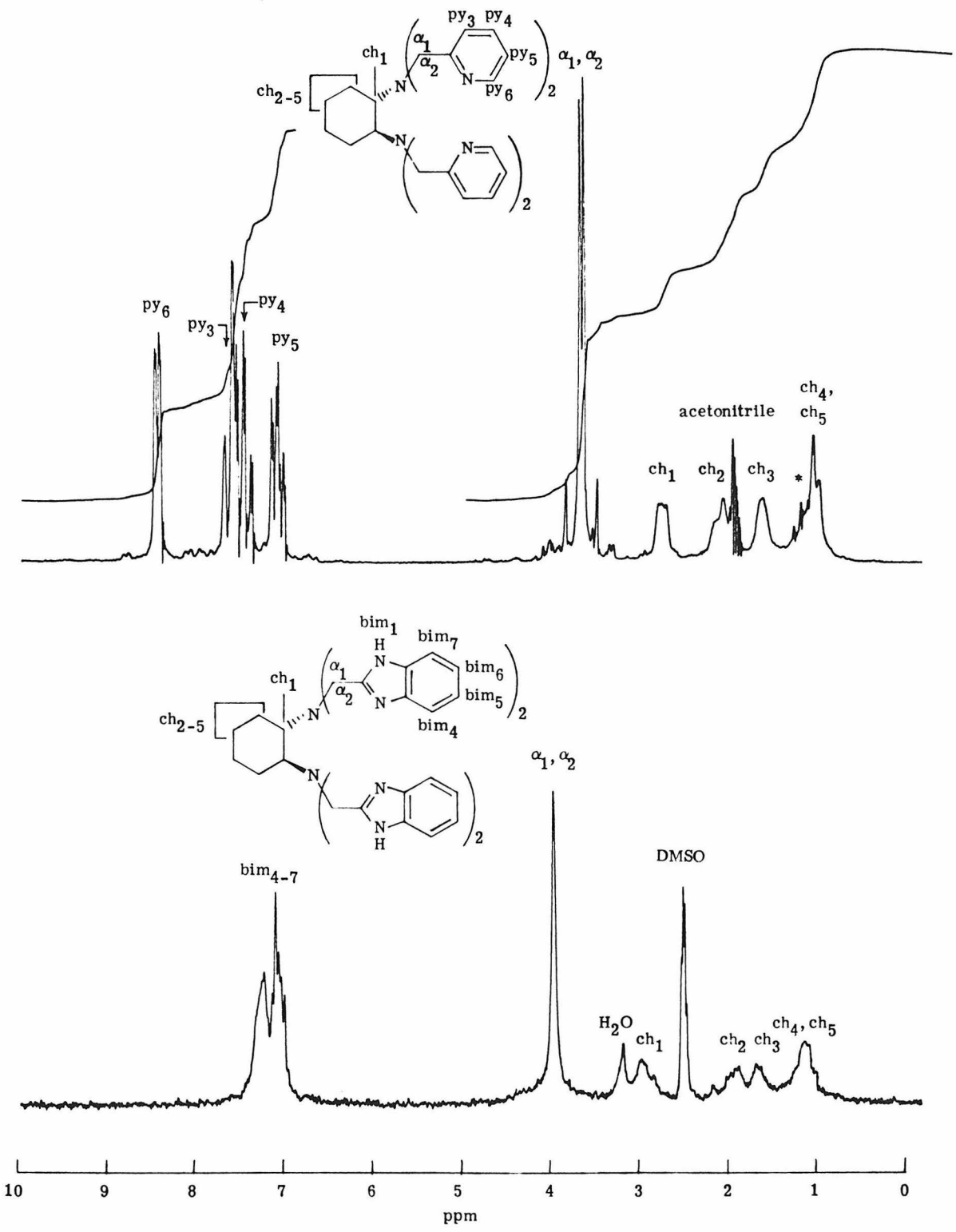


Figure 1. 90 MHz NMR spectra of CHXNpy (top) and CHXNbim (bottom) in CD_3CN and d_6-DMSO, respectively, at 34°C.

interchange process probably requires breakage and reformation of multiple copper-nitrogen bonds as well as amine nitrogen inversion and various rotations. In the slow-exchange limit the low (C_2) symmetry of cyclohexanediamine would be expected to produce two pairs of inequivalent heterocycles. (Another way of stating this is that slow inversion of amine nitrogen would cause the two attached pyridylmethyl or benzimidazolylmethyl groups to become diastereotopic.)

The higher resolution and faster time scale of 500 MHz spectra make it clear that two different types of heterocycles do, in fact, occur in each of the complexes. In the spectrum of $Cu_2(CHXNpy)(BF_4)_2$ in Figure 2 the two sets of pyridine absorptions are sharp and, for the most part, well resolved (although some reduction in temperature was necessary to achieve this). Similarly, there are four doublets which are attributable to the methylene protons, rather than two as in the spectrum of the uncomplexed ligand. As seen in Table I, resonances are shifted both upfield and downfield from their positions in the free ligand, and some of these shifts are quite large. The effect on the protons adjacent to the pyridine nitrogens (py_6) is particularly notable. In the complex the resonances of the two different pairs py_{6a} and py_{6b} are split by 1.09 ppm, with one resonance shifted 0.50 ppm upfield and the other 0.59 ppm downfield from the position in the uncomplexed ligand. Pyridine ring currents must play an important role in producing these shifts.[4]

Similar effects are evident in the 500 MHz spectrum of $Cu_2(CHXNbim)(BF_4)_2$ (Figure 3; in this case cooling was not necessary to achieve good resolution). It might be noted that the imidazole ring

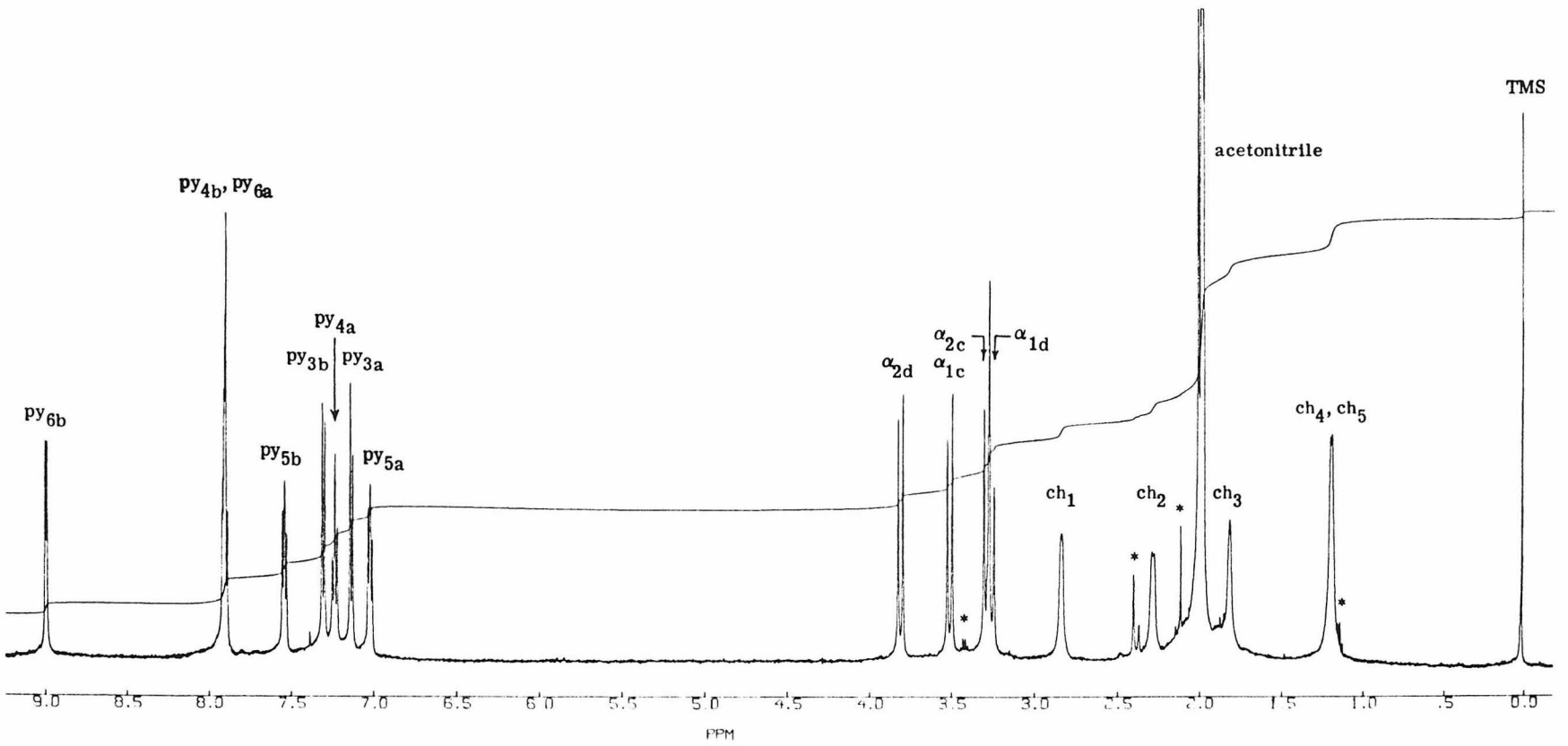


Figure 2. 500 MHz NMR spectrum of $Cu_2(CHXNpy)(BF_4)_2$ in CD_3CN at -30°C. The labeling scheme is illustrated in Figure 1. Alphabetic subscripts denote different pyridine or methylene groups. Assignments were confirmed by decoupling experiments. Asterisks denote solvent impurities.

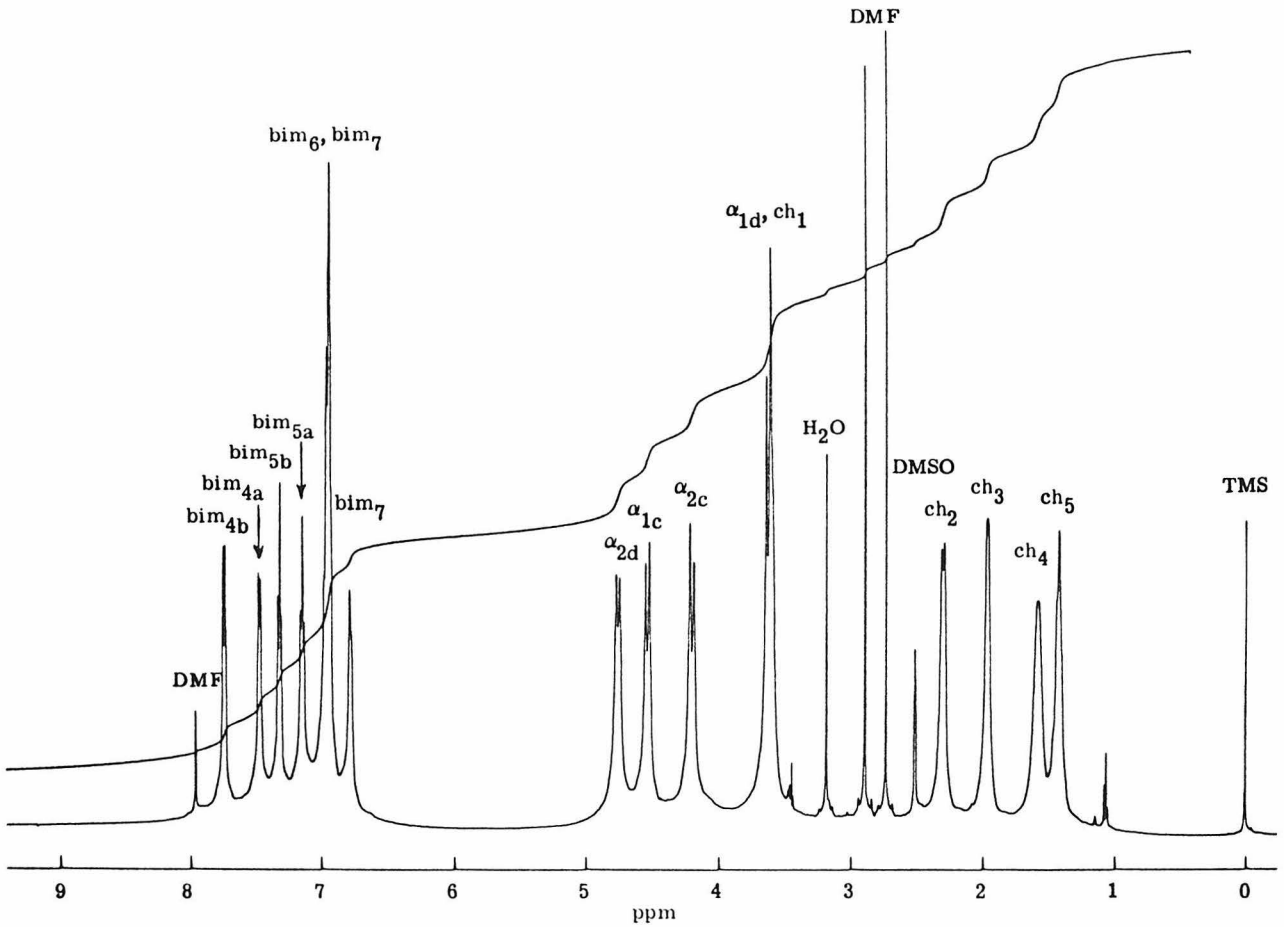


Figure 3. 500 MHz NMR spectrum of $Cu_2(CHXNbim)(BF_4)_2 \cdot \frac{1}{2}DMF$ in d_6-DMSO at 30°C. The labeling scheme is illustrated in Figure 1. Alphabetic subscripts denote different benzimidazole or methylene groups. Assignments were confirmed by decoupling experiments. The bim_1 peak appears at 13.16 ppm.

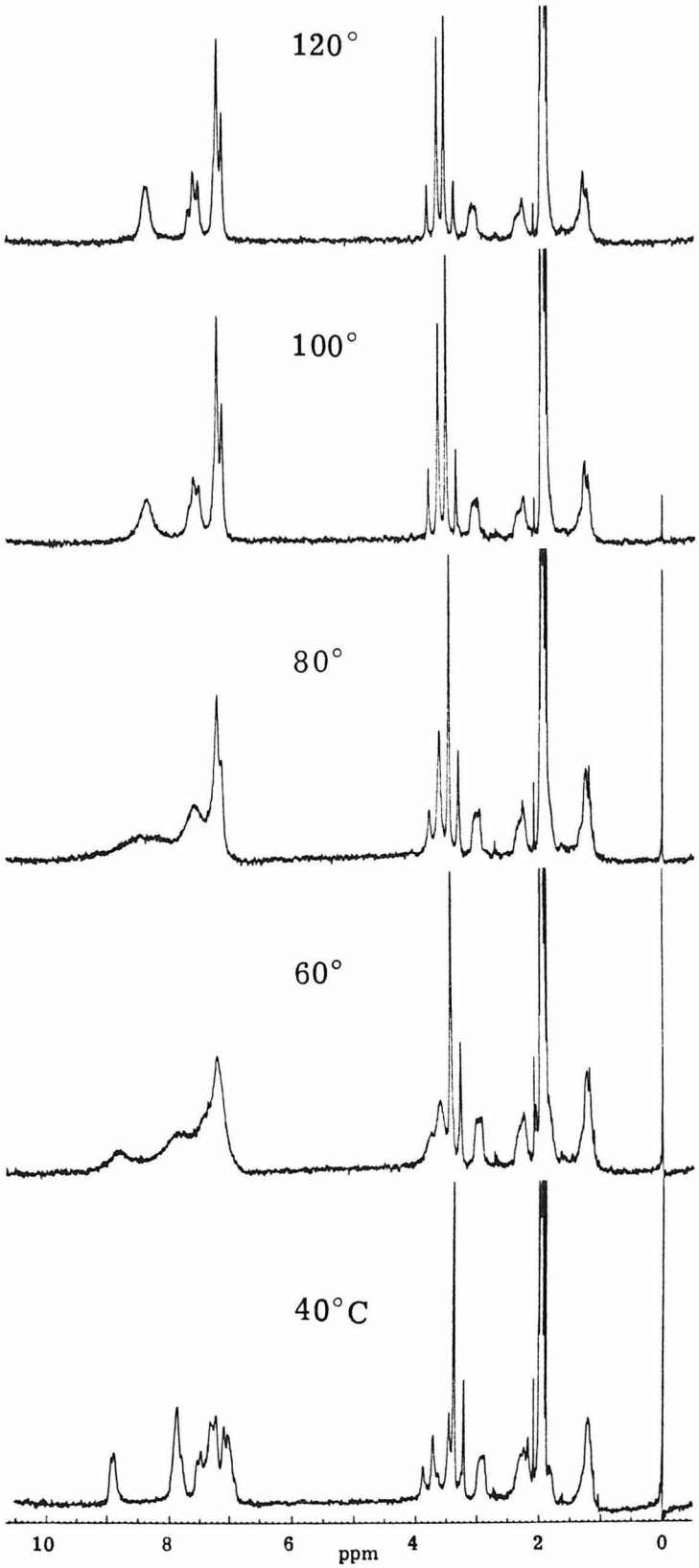


Figure 4. 90 MHz NMR spectra of $Cu_2(CHXNpy)(BF_4)_2$ in CD_3CN.

Table I. Proton NMR Chemical Shifts for Copper(I) Complexes and Ligands[a]

Compound	ch_1	ch_2	ch_3	ch_4	ch_5	α_1	α_2	py_3/ bim_4	py_4/ bim_5	py_5/ bim_6	py_6/ bim_7	bim_1
CHXNpy	2.73	2.06	1.27	(1.02)		3.57	3.69	7.60	7.42	7.04	8.39	
$Cu_2(CHXNpy)(BF_4)_2$[b]	2.82	2.27	1.80	(1.18)		3.49	3.27	7.12	7.22	7.00	7.89	
						3.24	3.79	7.29	7.89	7.52	8.98	
$Cu_2(CHXNpy)(BF_4)_2$[c]	3.06	2.28	(1.9)	(1.27)		3.48	3.69	(7.2)	7.59	(7.2)	8.35	
CHXNbim	2.94	1.90	1.65	(1.12)		3.96		(7.04, 7.22)				12.73
$Cu_2(CHXNbim)(BF_4)_2$[d]	3.60	2.30	1.96	1.58	1.42	4.53	4.20	7.47	7.14	(6.95)	6.77	13.16
$\cdot \frac{1}{2}$DMF						3.63	4.75	7.74	7.31			

[a]Chemical shifts are given in ppm, δ, relative to $SiMe_4$. Values in parentheses are approximate and correspond to overlapping peaks. The proton labeling scheme is illustrated in Figure 1. CHXNpy and its complex were dissolved in CD_3CN; the sample of the complex was sealed in an evacuated tube. CHXNbim and its complex were dissolved in d_6-DMSO under an atmosphere of helium. Ligand spectra were recorded on a 90 MHz instrument at 34°C. [b]500 MHz spectrum at -30°C. Resonances for different pyridylmethyl groups are listed on different lines; however, α_1 and α_2 resonances do not necessarily correspond to the same group as the py resonances. [c]90 MHz spectrum at 120°C. [d]500 MHz spectrum at 30°C. The assignments of bim_4 and bim_5 may be interchanged with bim_7 and bim_6, respectively. DMF: 2.73, 2.89, 7.95.

protons (bim_1) produce only a single absorption (not shown in Figure 3) in spite of the inequivalence of the benzimidazole groups. Thus, these protons probably exchange rapidly.

The stereochemical nonrigidity of $Cu_2(CHXNpy)^{2+}$ becomes most apparent if spectra are examined at elevated temperatures (Figure 4). Coalescence of the pyridylmethyl absorptions occurs at approximately 70°C, and the fast-exchange limit is not reached until well above 100°C (on the 90 MHz NMR timescale). The spectrum that results is similar to that of the free ligand, with a single set of pyridine resonances and an AB pattern ($J/\Delta\nu = 0.7$) for the α_1 and α_2 protons. Most of the absorptions are in about the same place or shifted downfield from their positions in the ligand spectrum, the primary exception being py_3, which is shifted upfield. (The spectrum of $Cu_2(TPEN)^{2+}$ is similar in this respect; see Chapter 2.) Throughout these temperature changes the cyclohexyl resonances remain nearly unaltered and similar to those of the uncomplexed ligand (except for downfield shifts). This suggests that the cyclohexane ring is locked in a single conformation. That expected to be most stable would be a chair conformation with both tertiary nitrogens in equatorial positions.

Reactivity with Carbon Monoxide and Oxygen

Green solutions of $Cu_2(CHXNpy)(BF_4)_2$ in DMF turn yellow upon exposure to carbon monoxide. This color change is accompanied by the appearance of a carbonyl stretching absorption in the infrared at 2087 cm^{-1}. (This compares to 2110 cm^{-1} for $Cu_2(TPEN)(BF_4)_2$ in dichloromethane.) Purging with nitrogen results in the return of a

green coloration. Unlike the colorless solutions of $Cu_2(TPEN)(BF_4)_2$ in CO-saturated DMF, solutions of $Cu_2(CHXNpy)(BF_4)_2$ are still subject to disproportionation in the presence of CO. Carbon monoxide does appear to slow the disproportionation, however, particularly at low temperatures. The presence of CO results in somewhat improved solubility and stability in certain other solvents at low temperature (e.g., acetone, dichloromethane), although disproportionation is still rapid in most solvents at room temperature. Nitromethane provides an exception to this; although the compound disproportionates immediately in this solvent under inert atmosphere, it dissolves to give a green solution in the presence of CO which may show little sign of disproportionation for minutes at 25°C or hours at -28°C (near freezing). (In any case a blue solution and copper metal are eventually formed.) $Cu_2(CHXNpy)(BF_4)_2$ does not react with carbon monoxide in acetonitrile solution, as indicated by the lack of any carbonyl absorption in the infrared.

Again, in contrast to the behavior of $Cu_2(CHXNpy)(BF_4)_2$ is that of $Cu_2(CHXNbim)(BF_4)_2$. The latter compound shows no qualitative changes in CO-saturated solvents. This lack of reactivity is confirmed by solution infrared spectroscopy (in DMF), as well as NMR spectroscopy (the proton spectrum shows no changes when a sample in d_6-DMSO is placed under CO atmosphere).

The reaction of $Cu_2(CHXNpy)^{2+}$ with carbon monoxide was of some interest in relation to the objective of forming bridging adducts. It seemed feasible that such an adduct of CO could be stabilized under appropriate circumstances. Copper complexes containing bridging carbonyl groups are rare, and only one such crystal structure has been reported.[5-7] (It is worth noting that this crystallographically charac-

terized complex is stable only in the solid state and in solution in non-polar solvents, in which it has poor solubility.[6]) In order to further characterize the carbonyl chemistry of $Cu_2(CHXNpy)^{2+}$, its ^{13}C NMR spectrum has been examined in the presence of ^{13}CO (90%). Low temperatures are necessary to slow the exchange of bound and unbound CO, as well as to prevent disproportionation. The spectrum at -88°C shows only one peak attributable to bound CO, at 169.8 ppm (vs. $SiMe_4$). A mixed solvent, 1:1 DMF/2-nitropropane, was used to achieve good solubility and fluidity at low temperatures. (The peaks are broadened due to exchange even at -88°C. For the 169.8 ppm peak, $\nu_{\frac{1}{2}} \approx 28$ Hz. Free CO appears at 173.1 ppm.) The spectrum of $Cu_2(TPEN)^{2+}$ (in d_6-acetone at -80°C) shows a corresponding peak at 173.5 ppm, with free CO appearing at 184.8. (These peaks become resolved at higher temperatures than for $Cu_2(CHXNpy)^{2+}$; some broadening of the 173.5 ppm peak is still evident, however, probably due to the quadrupole moment of copper.) These chemical shifts lie within a range expected for terminal CO.[8,9] Resonances of bridging carbonyl groups would be expected to appear farther downfield.[8] Thus, NMR data confirm the DMF solution infrared results for $Cu_2(CHXNpy)^{2+}$ in indicating the presence of only terminally-bound groups in its carbonyl adduct.

Initial attempts to isolate a carbonyl adduct were unsuccessful, apparently due to a lack of stability at room temperature. For example, evaporation of solutions of the complex in a stream of CO produces only starting material or disproportionation products, although this procedure does give a carbonyl adduct in the case of $Cu_2(TPEN)(BF_4)_2$. A carbonyl adduct of $Cu_2(CHXNpy)^{2+}$ was obtained at low temperature (-25°C), however, by precipitation from a nitro-

methane solution with ethyl acetate. The solid produced by this procedure is an off-white (slightly grayish) powder which slowly loses carbon monoxide in an inert atmosphere or under vacuum. It may be kept largely intact for a period of weeks if stored under carbon monoxide. The infrared spectrum of this material (Nujol mull, prepared under He) shows a single carbonyl stretching absorption at 2099 cm^{-1}, indicative of terminally-bound CO. As with $Cu_2(TPEN)(CO)_2(BF_4)_2$ (which has a pair of absorptions at 2097 and 2107 cm^{-1}), this band is at higher frequency than in most other copper carbonyls that have been isolated, and may indicate less than the usual extent of π-backbonding to CO (see Chapter 2 and references therein). Dissolution of the carbonyl adduct of $Cu_2(CHXNpy)(BF_4)_2$ in acetonitrile is accompanied by effervescence. The NMR spectrum of the resulting solution is identical to that of the starting complex. Quantitative collection of the gas evolved on dissolution indicates a stoichiometry of 0.95 ± 0.03 molecule of CO per copper ion. Thus, like $Cu_2(TPEN)^{2+}$, $Cu_2(CHXNpy)^{2+}$ forms a terminal dicarbonyl.

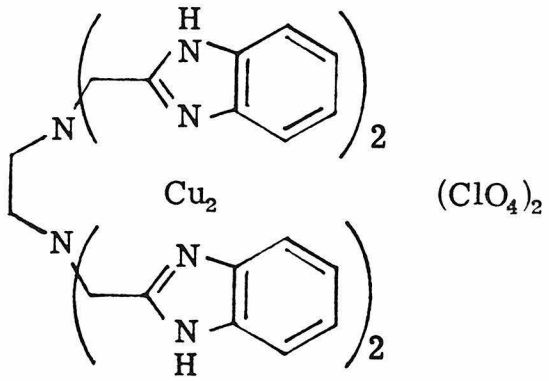
Regarding oxygen reactivity, neither $Cu_2(CHXNpy)(BF_4)_2$ nor $Cu_2(CHXNbim)(BF_4)_2$ shows any color or infrared spectral changes in the solid state if placed under dry oxygen for a period of days. Both compounds react with oxygen in solution, although the latter reacts much more slowly than the former. In both cases green solutions result which show no further color changes on purging with nitrogen or carbon monoxide or when placed under vacuum. The NMR spectrum of $Cu_2(CHXNbim)^{2+}$ in d_6-DMSO is the same under an atmosphere of He or O_2, although in the latter case the absorptions slowly broaden as the

complex reacts. The reaction of $Cu_2(CHXNpy)^{2+}$ with oxygen is also slow in some solvents (e.g., acetonitrile, acetone, dichloromethane) at low temperature, although the reaction with carbon monoxide remains rapid. In DMF the reaction with oxygen is not slowed as much at low temperature, but still shows no qualitative indications of reversibility. The stoichiometry was measured at 0.36 O_2/Cu in DMF at -40°C. It is possible that this value is somewhat low as a result of partial disproportionation of the sample. The same sample showed no further uptake of oxygen when warmed to 24°C. The products of the oxygen reactions of $Cu_2(CHXNpy)(BF_4)_2$ and $Cu_2(CHXNbim)(BF_4)_2$ have not been characterized.

The reaction of the dicarbonyl adduct of $Cu_2(CHXNpy)(BF_4)_2$ with oxygen in the solid state has also been examined. This material changes from off-white to blue under oxygen. The infrared spectrum of the product shows new bands at 452, 610, and ca. 650 cm^{-1}, tapering off to ca. 820 cm^{-1} (other bands are superimposed in this region). The carbonyl band is absent (except for a small remnant) and there is no significant absorption in the O-H stretching region. If this product is heated (to 60-80°C) in vacuo the color changes to green and the new infrared absorptions disappear, leaving a spectrum similar to that of $Cu_2(CHXNpy)(BF_4)_2$. However, no oxygen is evolved in this process (see Experimental Section). Also, it is significant that if moisture is carefully excluded during the reaction of the dicarbonyl with oxygen, this reaction may take weeks, whereas the color change to blue occurs within hours in air.

Discussion

The similarity of various properties of $Cu_2(CHXNpy)(BF_4)_2$ and $Cu_2(TPEN)(BF_4)_2$ suggests that these compounds have similar structures in the solid state. The structure of $Cu_2(CHXNbim)(BF_4)_2$ is probably also similar (but with significant differences), particularly in view of the recently published crystal structure of the analogous compound 1.[2,10] The structure of 1 is like that of $Cu_2(TPEN)^{2+}$, but



1

the coordination is more nearly linear and there is less, if any, direct copper-copper interaction (Cu-Cu = 3.04 Å). Furthermore, there are no copper-tertiary amine bonds in 1 (Cu-N = 2.77 Å; the nitrogen lone pairs are not aimed at the metals).

The substitution of cyclohexanediamine for ethylenediamine does clearly have a restraining effect on the solution structures of the complexes. This is evident in the reactivity as well as in the dynamic NMR spectra. A few other fluxional copper(I) complexes have been reported,[11-13] but coalescence usually occurs well below room

temperature rather than well above, as with these complexes. The presence of cyclohexanediamine rather than ethylenediamine in $Cu_2(CHXNpy)^{2+}$ does seem to have some stabilizing effect on the complex in the absence of other ligands, although this appears to be largely a kinetic rather than a thermodynamic effect. The greater bulk and more tightly closed structure of $Cu_2(CHXNpy)^{2+}$ may simply slow the intermolecular process that leads to disproportionation,[14] so that this does not occur as rapidly as in $Cu_2(TPEN)^{2+}$. On the other hand, the extra restraint of cyclohexanediamine destabilizes the carbonyl adduct. Apparently the complex must adopt a more open conformation in order for each metal ion to bind a molecule of carbon monoxide. It is possible with a space-filling molecular model to orient the ligand so that the metal ions face away from one another, but this structure appears to be quite strained. Evidently as a result of such strain, the carbonyl adduct is not sufficiently stable to prevent disproportionation, as with $Cu_2(TPEN)^{2+}$. Also, in contrast to $Cu_2(TPEN)(CO)_2(BF_4)_2$, $Cu_2(CHXNpy)(CO)_2(BF_4)_2$ loses CO fairly readily in the solid state. The restraining effect of cyclohexanediamine is also evident in the reactivity of $Cu_2(CHXNbim)^{2+}$; whereas this complex does not react with carbon monoxide, compound $\underset{\sim}{1}$ does (ν_{CO} = 2065 cm^{-1} in DMSO solution[10]).

The slow reactivity with oxygen of $Cu_2(CHXNbim)^{2+}$ at room temperature and of $Cu_2(CHXNpy)^{2+}$ at low temperature in some solvents suggests that the complexes are too restrained or hold the copper ions too close together to form stable bridging dioxygen adducts. $Cu_2(CHXNpy)^{2+}$ is not too restrained to bind terminal carbonyl ligands

rapidly under the same conditions, so a different mode of binding for oxygen might explain the low reactivity. The reaction stoichiometry of 0.36 O_2/Cu for $Cu_2(CHXNpy)^{2+}$ in DMF suggests that binding of oxygen to copper occurs under the conditions of the measurement, but with subsequent irreversible reaction. The value 0.36 may be low (due to disproportionation as a side reaction) but does indicate reaction beyond the simple four-electron reduction of O_2 by four copper(I) ions. A stoichiometry of 0.5 O_2/Cu would be consistent with oxidation of the copper ions plus monohydroxylation of the ligand, possibly at one of the methylene carbons or pyridine rings. There are precedents for such hydroxylations.[15,16]

The nature of the blue product formed by $Cu_2(CHXNpy)(CO)_2(BF_4)_2$ in oxygen is not clear. The fact that water is implicated in the reaction and that the product does not evolve O_2 suggests that the blue material is not a dioxygen adduct. Also, the new infrared absorptions of this material (for the most part) do not lie in the range expected for O–O stretching vibrations ($\sim$ 800-900 cm^{-1} for peroxo complexes[17,18]).

The properties of $Cu_2(CHXNpy)^{2+}$ and $Cu_2(CHXNbim)^{2+}$ imply that benzimidazole is a better ligand than pyridine for stabilizing low coordination numbers of copper(I). The properties of $Cu_2(TPEN)^{2+}$ and compound $\underset{\sim}{1}$ are also consistent with this; $\underset{\sim}{1}$ does not disproportionate in solution. This difference in stability with respect to disproportionation does not appear to be attributable to an inability of the tetrabenzimidazole ligands to form stable mononuclear copper(II) complexes. A crystal structure of such a complex of the ligand in compound $\underset{\sim}{1}$ has been reported; all six nitrogens are bound to Cu(II)

(although the Cu-N(amine) distances are long, 2.50 Å). The tendency of copper(I) to form two-coordinate complexes with strong σ-donors and four-coordinate complexes with strong π-acceptors has been noted.[19] Where coordination to copper(I) is concerned, imidazole appears to fall into the former category and pyridine into the latter.[19] Imidazole and benzimidazole are stronger bases than pyridine (pK_a 7.0, 5.5, and 5.2, respectively[20]). This may be rationalized in terms of resonance structures for the former which allow distribution of positive charge over two nitrogen atoms. While the σ and π electronic properties of benzimidazole are intermediate between those of imidazole and pyridine, comparison of the structures of $Cu_2(TPEN)^{2+}$ and $\underset{\frown}{1}$ strongly suggests that ligation by benzimidazole fosters two-coordination.

Experimental Section

Materials. All chemicals were reagent grade and were used as received unless otherwise noted. Reagent grade N,N-dimethylformamide (DMF) was dried over activated 4A molecular sieves for 48 hours and then vacuum distilled from additional sieves. Aldrich spectrophotometric grade (99%) nitromethane was used without further purification. Acetonitrile, acetone, and dichloromethane (spectroscopic grade) for vacuum-line oxygen reactions were stored over 4A sieves, calcium sulfate, and calcium hydride, respectively (with CH_2Cl_2 shielded from light), and vacuum transferred prior to reaction. Racemic trans-1,2-diaminocyclohexane was separated from a mixture of the cis and trans isomers according to a literature procedure.[21] o-Phenylenediamine was recrystallized twice from toluene before use. Tetra(acetonitrile)copper(I) tetrafluoroborate was prepared according to a literature method.[22]

N,N,N′,N′-Tetrakis(2-pyridylmethyl)-trans-1,2-cyclohexanediamine (CHXNpy). Picolyl chloride hydrochloride (7.96 g, 48.5 mmole), trans-1,2-diaminocyclohexane dihydrochloride (4.54 g, 24.3 mmole), and water (2.6 ml) were placed in a three-neck round-bottom flask which was subsequently purged with nitrogen. To the resulting mixture was added, with stirring, 18.0 ml of 5.4 N NaOH (97.0 mmole). The resulting red emulsion was stirred under nitrogen for ten days. During this period additional picolyl chloride hydrochloride (a total of 9.95 g, 60.7 mmole) was added in three portions as well as sufficient 5.4 N NaOH (added more frequently) to keep the mixture basic but below pH 9.5. The mixture was then extracted with

dichloromethane (3 × 50 ml) and the combined extracts were dried over sodium sulfate. After filtration the solvent was removed by rotary evaporation. The resulting oil was dissolved in a small amount of toluene and purified in 1.5-2 g. portions by flash chromatography[23] on an alumina column of 4.5 cm diameter (eluant, 7:3 ethyl acetate/pet ether (35-60)). The ligand was obtained as a pale yellow oil (4.1 g, 35%).

N,N,N′,N′-Tetrakis(2-benzimidazolylmethyl)-trans-1,2-cyclohexanediamine (CHXNbim). A mixture of trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid monohydrate (4.36 g, 12.0 mmole) and o-phenylenediamine (5.18 g, 47.9 mmole) was ground and intimately mixed. This powder was then placed in a round-bottom flask and heated to 200°C in an oil bath. As the reaction proceeded, steam was evolved and the initially molten mixture slowly solidified. Heating was continued for 10 min after the reaction appeared complete. The resulting cake was broken up and recrystallized twice from 1:1 pyridine/methanol to yield a white microcrystalline solid. Anal. ($C_{38}H_{38}N_{10}$) C, H, N.[24]

$Cu_2(CHXNpy)(BF_4)_2$. The synthesis of this material was performed under helium in a Vacuum Atmospheres Dri-Lab inert atmosphere chamber. The ligand CHXNpy (0.91 g, 1.90 mmole) was dissolved in acetonitrile (ca. 10 ml) and $Cu(CH_3CN)_4BF_4$ (1.20 g, 3.80 mmole) was added. Almost all of the solvent was removed from this solution in vacuo, to produce an oily residue (some $Cu(CH_3CN)_4BF_4$ tends to crystallize in this process). Methanol (ca. 9 ml) was then added, which induced the precipitation of microcrystalline product.

After ca. 1 min of stirring, the material was collected on a frit by suction filtration, washed with two small portions of methanol, and dried in vacuo for 30 min. This yielded 0.92 g (62%) of yellowish green product. A second crop (0.20 g) of more greenish material was obtained by removing the solvent from the filtrate in vacuo, dissolving the residue in acetonitrile and repeating the above procedure. Anal. ($C_{30}H_{34}B_2Cu_2F_8N_6$) C, H, N, Cu.

$Cu_2(CHXNbim)(BF_4)_2 \cdot \frac{1}{2}DMF$. This synthesis was also performed under helium. To a slurry of the ligand CHXNbim (0.500 g, 0.788 mmole) in DMF (ca. 4 ml) was added $Cu(CH_3CN)_4BF_4$ (0.496 g, 1.58 mmole), which resulted in complete dissolution of the ligand. To this solution absolute ethanol (ca. 15 ml) was added dropwise, with stirring. This resulted in precipitation of white microcrystalline product, which was collected on a frit, washed twice with ethanol and ether, and dried in vacuo for 30 min. Yield: 0.65 g (85%). Anal. ($C_{39.5}H_{41.5}B_2Cu_2F_8N_{10.5}O_{0.5}$) C, H, N, Cu.

$Cu_2(CHXNpy)(CO)_2(BF_4)_2$. $Cu_2(CHXNpy)(BF_4)_2$ (0.20 g) was transferred (under helium) along with a magnetic stir bar, into one of two round-bottom side-arm flasks connected by a Schlenk frit. This apparatus was connected to a vacuum line and evacuated, and nitromethane (ca. 3 ml) was vacuum transferred into the flask containing the complex. The apparatus was then filled with an atmosphere of CO and the solvent was thawed with the flask immersed in an ethanol/water slush bath at -25°C. After all of the solid had dissolved, the resulting green solution was frozen again, the apparatus was evacuated, and ethyl acetate (ca. 12 ml) was vacuum transferred into the flask. After the apparatus had been refilled with CO, the solvent was thawed at

-25°C, resulting in precipitation of an off-white solid. The apparatus was removed from the vacuum line, transferred to a fume hood, and then inverted. The mixture was filtered under CO pressure, and the product collected on the frit was washed with cold (0°C) CO-saturated ethyl acetate and then dried under a stream of CO for 70 min.

To determine the CO content of this material, an approximately 50 mg sample was transferred (in air) to a preweighed 10 ml round-bottom flask and quickly weighed on an analytical balance. The flask was then connected to a vacuum line, immersed in liquid nitrogen, and quickly evacuated. Following this the flask was warmed to room temperature and any gas evolved collected by means of a Toepler pump, after passing through two liquid nitrogen traps. The evolution of gas was slow, so the flask was again immersed in liquid nitrogen, and after all CO had been collected, acetonitrile was vacuum transferred into the flask. The flask was then closed off and warmed to room temperature. Dissolution of the solid was accompanied by effervescence. The resulting deep yellow solution was frozen in liquid nitrogen, the flask was opened to the system and collection of gas with the Toepler pump was resumed. The solution was completely degassed after three freeze-pump-thaw cycles. Measurement of the pressure and temperature of the gas, which had been collected in a calibrated volume, indicated that 0.95 ± 0.03 mole had been evolved per mole of copper (assuming a formula of $Cu_2(CHXNpy)(CO)_2(BF_4)_2$ for the original sample).

Oxygen reaction of $Cu_2(CHXNpy)(CO)_2(BF_4)_2$. A sample of $Cu_2(CHXNpy)(CO)_2(BF_4)_2$ was quickly transferred (in air) to a small

flask which was then sealed with a septum cap and purged with oxygen (passed through a calcium sulfate drying tube). The flask was then placed in a dessicator for three weeks, during which the sample slowly turned blue. (The color change occurs more rapidly if less care is taken to exclude moisture.) About 30 mg of the blue material was transferred to a preweighed flask, quickly weighed, and connected to a vacuum line. After the flask (temporarily immersed in liquid nitrogen) had been evacuated, heating of the sample was begun, with evolution of gas monitored by means of a Toepler pump. The sample was heated to a maximum of 80°C and some gas was collected (slow evolution of gas began at ca. 60°C). However, mass spectral analysis of the gas showed that it was entirely CO, with no more than normal background oxygen (a fraction of a percent of the amount of CO).

Oxygen uptake of $Cu_2(CHXNpy)(BF_4)_2$. A small flask containing ca. 0.08 mmole of complex (weighed in air) was connected to an 8 ml calibrated volume apparatus on a vacuum line and evacuated. DMF (ca. 4 ml) was vacuum transferred into the flask, which was then closed from the rest of the apparatus. With the sample kept frozen, the calibrated volume was filled with a measured pressure of oxygen (ca. 450 Torr), the temperature was noted, and the calibrated volume was closed off. The flask was then opened to the calibrated volume and the solvent was thawed with the flask immersed in a methanol/water slush bath kept at -40 ± 2°C. The solution was stirred for 110 min. At the end of this period the solution was frozen in liquid nitrogen and the oxygen that remained was collected by means of a Toepler pump, after passing through two liquid nitrogen traps. The reaction solution

was completely degassed after three freeze-pump-thaw cycles. The amount of oxygen consumed was calculated by difference. (A small amount of copper metal was noted in the flask, indicating some disproportionation occurred.) The above procedure was repeated with the same sample, but with reaction at 24° rather than -40°C. Oxygen consumption in this second experiment was measured at 0.02 ± 0.02 O_2/Cu.

Physical Measurements. Samples of the copper(I) complexes for physical studies were prepared under helium in a Vacuum Atmospheres Dri-Lab inert atmosphere chamber.

Routine proton magnetic resonance spectra were recorded on a Varian EM-390 spectrometer at 90 MHz (34°C). Carbon-13 and most temperature-dependent proton NMR spectra were recorded on a JEOL FX90Q spectrometer. A Bruker WM500 spectrometer was employed for 500 MHz spectra.

Infrared spectra were recorded on a Beckman IR 4240 spectrophotometer. Solid-state samples were prepared as Nujol mulls, pressed between KBr plates. Solution samples were prepared by placing the solid complex under CO, adding CO-saturated solvent, and transferring the solution via a cannula to a solution cell (CaF_2, 1 mm path) sealed with septum caps.

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CHAPTER 4

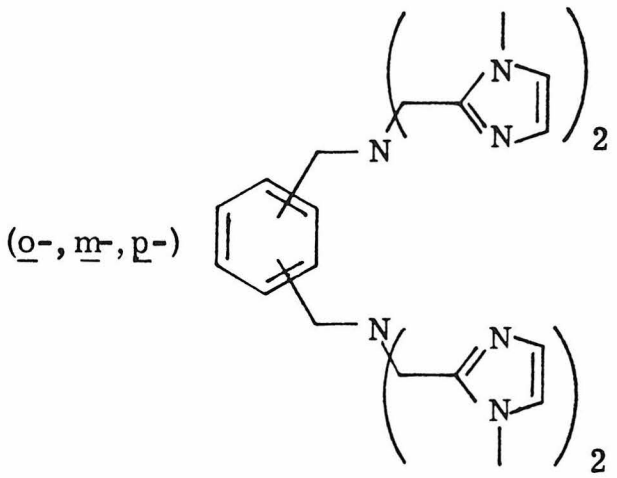
Synthesis and Reactivity of Binuclear Copper(I) Complexes of N,N,N′,N′-Tetrakis(1-methylimidazol-2-ylmethyl)-α,α′-diaminoxylenes

Introduction

The complexes in the preceding chapter provide a clear example of the differences in reactivity that can result from the substitution of one nitrogenous heterocycle for another in otherwise similar copper(I) complexes. This is not the only such example (vide infra).[1-4] In response to observed reactivity differences, or perhaps in anticipation of them, there has recently appeared in the literature[1-7] an increased amount of discussion of the advantages and disadvantages of various heterocycles as models for the imidazoles that occur in biological systems (see Chapter 1). A variety of copper complexes containing pyridine, pyrazole, and benzimidazole have been synthesized. However, there have been very few attempts at preparing binucleating ligands containing imidazole itself, especially ones that can provide more than one imidazole group per copper. Extensive attempts were made in our laboratories[8,9] to prepare a tetrakis(1-methylimidazolyl) version of the complexes in the Appendix of this thesis. Unfortunately, these efforts were unsuccessful due to difficulties encountered in the ligand synthesis.

The complexes to be discussed in this chapter are formed from the ligands illustrated schematically below. They are the first synthetic

copper(I) complexes of binucleating ligands with two simple imidazole



o-XYNmim
m-XYNmim
p-XYNmim

groups per metal ion. As with the TPEN ligand (Chapter 2), each copper ion bound by these ligands should be able to adopt a pseudo-tetrahedral geometry upon occupation of a fourth coordination site by another molecule. In this case, however, different xylyl "backbones" were chosen to allow variation of the copper-copper distance while still permitting the fourth coordination sites on the two metals to face one another.

Binuclear copper(I) complexes of a few other xylyl-bridged ligands have been reported. Osborn's "ear-muff" complex, which was reported to react reversibly with oxygen in the solid state, contains a p-xylyl group.[10,11] Recently, communications have appeared concerning two complexes similar to Cu_2(m-XYNmim)$(BF_4)_2$, discussed in this chapter, but with pyridine and pyrazole groups, respectively.[1-3] Reaction of the pyridyl complex with oxygen results in hydroxylation of the benzene ring. Comparison with these complexes will be made in the material that follows.

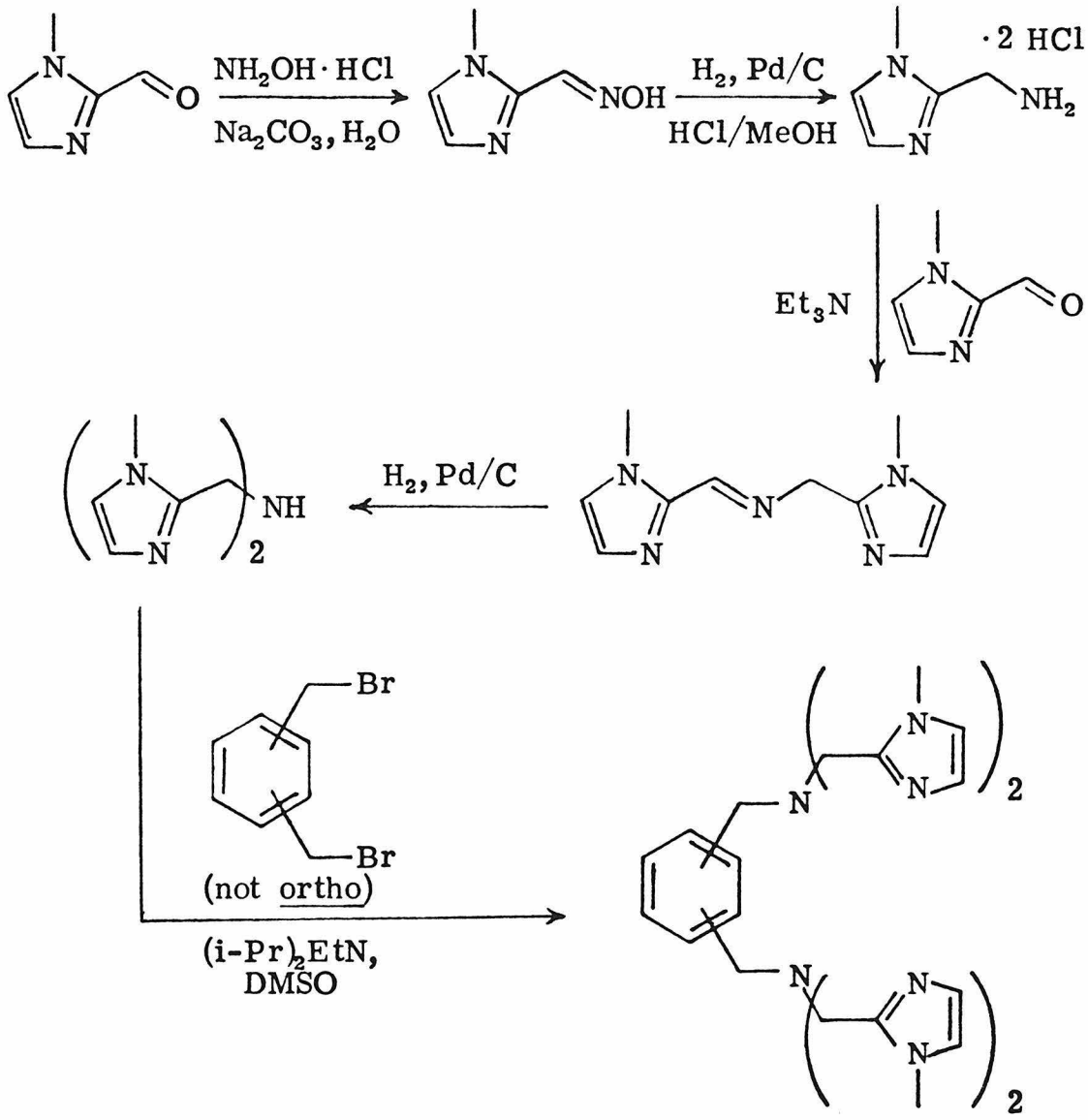
Synthesis of Ligands

Various attempts to prepare the ligands by procedures analogous to those used for TPEN and CHXNpy (Chapter 3) were unsuccessful. Small amounts were produced by reaction of 1-methyl-2-chloromethylimidazole hydrochloride with xylylenediamine in dimethylsulfoxide in the presence of the non-nucleophilic base N,N-diisopropylethylamine. The very low yield was probably due, ultimately, to alkylation of imidazole ring nitrogens at a rate competitive with alkylation of amine.

The procedure that was used with success in the preparation of the meta- and para-xylyl ligands is shown in Scheme 1. The procedure first requires the synthesis of the compound bis(1-methylimidazol-2-ylmethyl)amine. This was obtained as a crystalline solid after hydrogenation of the Schiff base formed in situ from 1-methyl-2-imidazolecarboxaldehyde and 1-methyl-2-aminomethylimidazole. Condensation of two equivalents of this secondary amine with α,α'-dibromoxylene (meta or para) gives the desired ligand. In the polar, aprotic solvent DMSO, with diisopropylethylamine added to absorb the acid produced, this last step proceeds rapidly with mild evolution of heat. The NMR spectra of the two ligands are similar and confirm their structures (Figure 1 and Table I).

If this procedure is carried out with α,α'-dibromo-o-xylene, only half of the bis(imidazolylmethyl)amine reacts. This stoichiometry and the NMR spectrum of the product are consistent with the formation of a cyclic quaternary ammonium salt, via intramolecular nucleophilic attack by tertiary amine following substitution for the first bromide.

Scheme 1

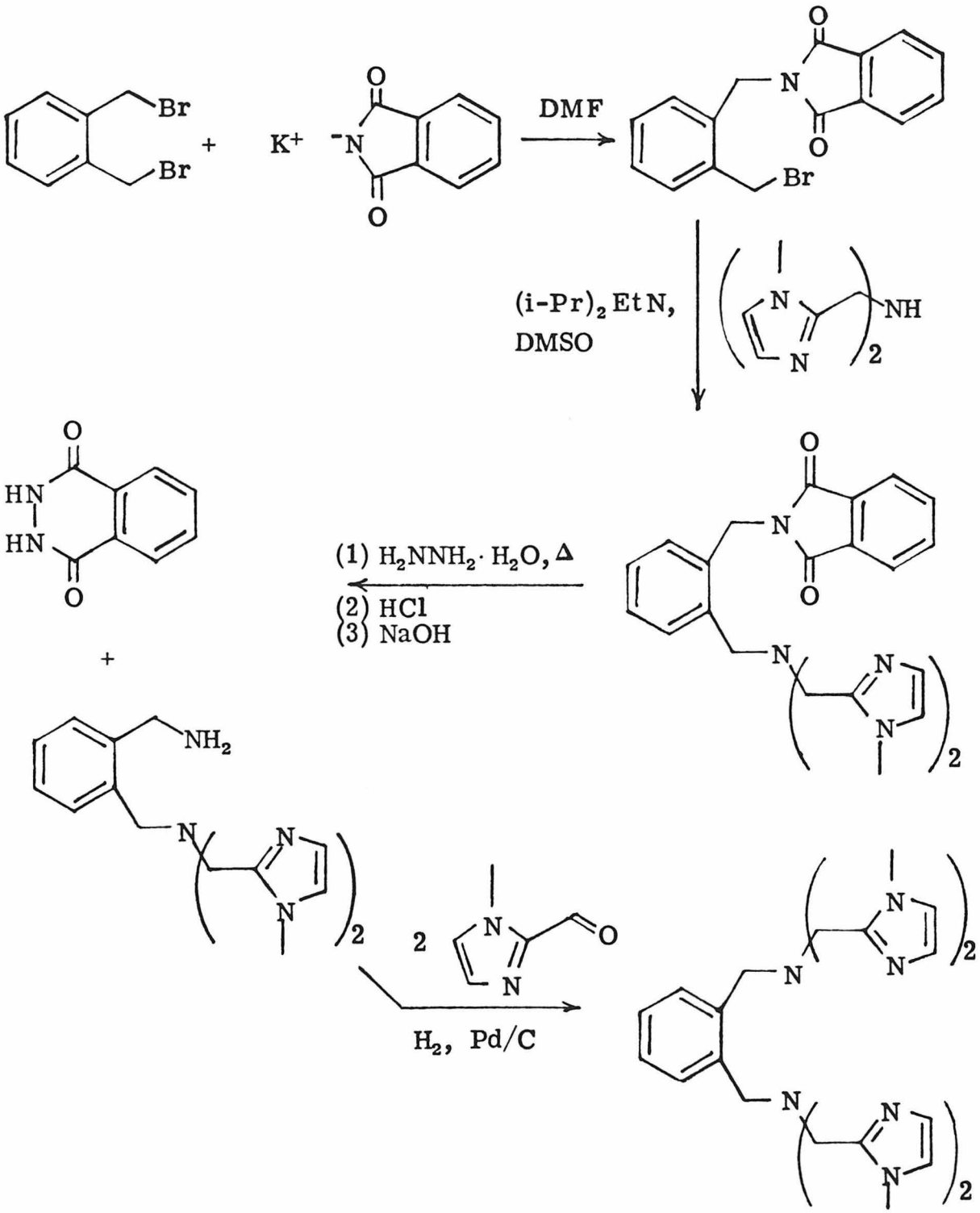

NH2OH·HCl
Na2CO3, H2O
NOH
H2, Pd/C
HCl/MeOH
·2 HCl
NH2
Et3N
O
NH
2
H2, Pd/C
Br
Br
(not ortho)
(i-Pr)2EtN,
DMSO
2
2

The NMR spectrum of the reaction mixture shows no evidence of the desired tetraimidazole product, even when excess secondary amine is used.

It had been hoped that formation of the desired product would be facilitated by including a metal ion in this reaction, so as to utilize a kinetic template effect (conversion of the second attack by a secondary amine center from an intermolecular to an intramolecular process). However, attempts using various metal ions were unsuccessful. The results of other purely organic approaches to the synthesis may be summarized by saying that there is a strong tendency toward cyclization in intermediate compounds whenever permitted by the functional groups involved.

The procedure that was used successfully avoided this problem by utilizing a phthalimide protecting group. The synthesis is summarized in Scheme 2. The first step is a mildly exothermic reaction when conducted in DMF, giving a statistical mixture of monophthalimide and diphthalimide products and unreacted dibromide starting material; from this the desired monophthalimide may be separated on the basis of solubility difference. The first two imidazole groups are introduced by reaction of this material with bis(imidazolylmethyl)amine, as before. The phthalimide group is then removed by hydrazinolysis, giving a primary amine "half ligand". The last two imidazole groups are attached to this in a single step by reductive alkylation with imidazolecarboxaldehyde. This avoids any quaternization of either amine or ring nitrogens. The 1-methyl-2-imidazolecarboxaldehyde itself is relatively resistant to reduction under the conditions employed, so that a good yield can be

Scheme 2



obtained without using a large excess of this material. The ligand is finally obtained as a colorless, crystalline solid whose NMR spectrum is similar to those of the meta- and para-xylyl ligands (Table I).

Synthesis and Characterization of Complexes

Binuclear copper(I) complexes of all three ligands were prepared in the same manner under inert atmosphere, by adding tetra(acetonitrile)copper(I) tetrafluoroborate in methanol to a methanol solution of the ligand. All three complexes were obtained as white powders, and all gave satisfactory elemental analyses. The complexes are only slightly soluble in methanol, acetone, and dichloromethane, but have good solubility in acetonitrile and dimethylformamide. In all cases colorless solutions result which show no signs of disproportionation. (Slight evidence of disproportionation was sometimes observed during the synthesis of Cu_2(o-XYNmim)$(BF_4)_2$, but the isolated complex gives stable solutions.)

Solid-state infrared spectra of the complexes show no splitting of absorptions due to the tetrafluoroborate anions, indicating that these are not bound to copper. Since both elemental analysis and NMR indicate the absence of solvent molecules, the copper ions presumably are either two- or three-coordinate in the solid state.

All complexes give NMR spectra with sharp resonances (Figure 1),

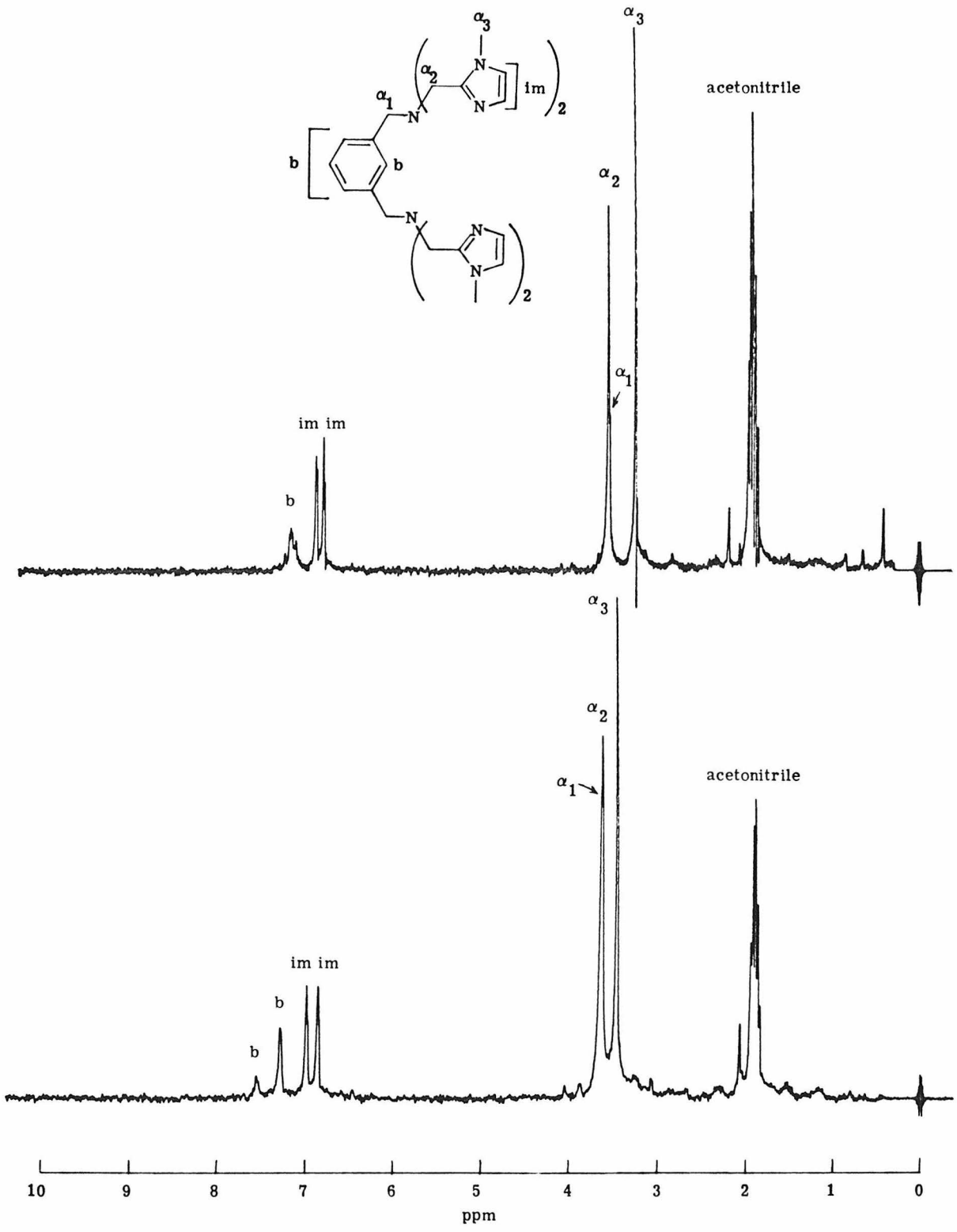


Figure 1. 90 MHz NMR spectra of m-XYNmim (top) and Cu_2(m-XYNmim)$(BF_4)_2$ (bottom) in CD_3CN at 34°C.

Table I. Proton NMR Chemical Shifts for Copper(I) Complexes and Ligands[a]

Compound	α_1	α_2	α_3	im[b]	b
o-XYNmim · $1.5H_2O$[c]	3.31	3.36	3.12	6.76, 6.86	7.18[d]
Cu_2(o-XYNmim)$(BF_4)_2$	3.82	3.61	3.44	6.83, 6.93	~7.22[e]
m-XYNmim	3.51	3.53	3.23	6.75, 6.83	7.10[e]
Cu_2(m-XYNmim)$(BF_4)_2$	3.65[f]	3.63	3.48	6.85, 6.98	7.27, 7.54[g]
p-XYNmim	3.51	3.53	3.26	6.75, 6.83	7.14
Cu_2(p-XYNmim)$(BF_4)_2$	3.64	3.60	3.45	6.89, 6.95	7.33

[a]All spectra were obtained in CD_3CN solution at 34°C under an atmosphere of helium. Chemical shifts are given in ppm, δ, relative to $SiMe_4$. The proton labeling scheme is illustrated in Figure 1. [b]Each value listed corresponds to a doublet. [c]Water appears at 2.23 ppm. [d]Broad. [e]Multiplet. [f]Shoulder. [g]The downfield peak has one-third the area of the upfield peak and probably corresponds to the proton in the 2 position.

confirming their diamagnetism. As indicated by Table I all resonances are shifted downfield in the complexes, relative to the free ligands, as a result of binding of the copper(I) ions.[12] Of the two different types of methylene protons, the α_1 protons (adjacent to the benzene ring, Figure 1) are affected to the greater extent in all cases, causing the α_1 and α_2 resonances to swap positions. This is particularly noticeable for the ortho-xylyl complex.

Reactivity with Carbon Monoxide and Oxygen

All complexes were found to form reversible adducts with carbon monoxide. This was expected since the relatively flexible ligands facilitate the adoption of a pseudotetrahedral geometry by the copper ions. The complexes generally show improved solubility in polar solvents in the presence of carbon monoxide, giving colorless solutions. Removal of CO from solutions in methanol or dichloromethane by purging with argon results in reprecipitation.

Solutions of the complexes in carbon monoxide-saturated DMF all show similar CO stretching absorptions in the infrared. These occur at 2079, 2074, and 2075 cm^{-1} for the ortho-, meta-, and para-xylyl complexes, respectively. These frequencies are lower than those observed for $Cu_2(TPEN)(CO)_2(BF_4)_2$ (2110 cm^{-1} in CH_2Cl_2) and $Cu_2(CHXNpy)(CO)_2(BF_4)_2$ (2087 cm^{-1} in DMF), and are more in accord with the values that have been observed for most other terminal

copper(I) carbonyls.[1,10,13-17] The shift to lower frequencies relative to the tetrapyridyl complexes probably reflects the stronger σ-donor character of imidazole, which would increase the electron density on copper and the extent of back-bonding to CO. The carbonyl adducts of these tetraimidazole complexes have not been isolated.

All of the complexes turn blue upon exposure to air in the solid state. On exposure to dry oxygen, however, powdered samples of $Cu_2(\underline{o}\text{-XYNmim})(BF_4)_2$ and $Cu_2(\underline{p}\text{-XYNmim})(BF_4)_2$ are virtually unaffected for a period of days, as indicated by little or no color change and no change in their infrared spectra. Solid $Cu_2(\underline{m}\text{-XYNmim})(BF_4)_2$ changes from white to dull green under dry oxygen, but there are only minor changes in its infrared spectrum. The color change is not reversed by heating the solid to 80°C under dynamic vacuum.

The complexes all react rapidly with oxygen in solution. These reactions were examined in acetonitrile, dimethylformamide, and dichloromethane (although reaction in the last of these is generally limited by the low solubility of the complexes), both at room temperature and low temperature (-30 to -78°C, depending on the melting point of the solvent). $Cu_2(\underline{m}\text{-XYNmim})(BF_4)_2$ typically reacts to give dark blue solutions, while $Cu_2(\underline{p}\text{-XYNmim})(BF_4)_2$ gives dark blue-green or green solutions. In no case was any further color change observed upon degassing solutions of these compounds, by freeze-pump-thaw cycles or by purging with argon or carbon monoxide, or in the case of the low-temperature reactions by warming to room temperature while degassing. The ortho-xylyl complex shows somewhat different behavior in that products of different colors are formed at different temperatures.

Solutions of the complex in acetonitrile, DMF, or dichloromethane react with oxygen at room temperature to give a green coloration. Reaction at low temperature produces a blue solution, which upon warming, with or without degassing, turns green at approximately 0° C. The green coloration is maintained if the temperature is lowered again. However, whether the reaction is conducted at room temperature or low temperature, the observed stoichiometry in CH_3CN is 0.25 ± 0.02 O_2/Cu. A similar statement applies for the meta- and para-xylyl complexes. This implies that the overall reaction is the four-electron reduction of O_2 by two binuclear copper(I) complexes.

The oxygen reaction of the meta-xylyl complex was of particular interest in view of the reaction mentioned in the Introduction, of a similar complex containing four pyridine groups.[3] In this latter reaction the benzene ring is hydroxylated in the 2 position (see Discussion section). That such a reaction does not occur in the case of Cu_2(m-XYNmim)$(BF_4)_2$ is implied by the above stoichiometry, which allows only for oxidation of the copper ions, not the ligand. The electronic absorption spectrum of the blue product lacks a band which appears at 390 nm in hydroxylated products,[1] which has been assigned to a phenoxide to Cu(II) charge transfer. Furthermore, if the copper is removed from an oxygenated solution of Cu_2(m-XYNmim)$(BF_4)_2$ by treatment with sodium sulfide, the ligand may be recovered largely unchanged, as indicated by its NMR spectrum (which is very similar to that of starting ligand, although broadened due, at least in part, to remaining traces of copper(II)). The dark blue solid obtained by removal of the solvent

from an oxygenated CH_3CN or DMF solution shows no O-H stretching absorptions in the infrared. This material may be recrystallized from CH_3CN/CH_3OH to give a blue solid whose elemental analysis and infrared spectrum are consistent with its formulation as an oxide or oxide-methoxide, $Cu_2(\underline{m}\text{-XYNmim})(O)(BF_4)_2 \cdot CH_3OH \cdot \frac{1}{2}H_2O$ or $Cu_2(\underline{m}\text{-XYNmim})(O)_{\frac{1}{2}}(OCH_3)(BF_4)_2 \cdot H_2O$. (Although infrared spectra of the recrystallized material generally showed absorptions (at ~3560-3610 cm^{-1}) in the O-H stretching region, these bands were absent if the material was first dried extensively in vacuo and the spectral sample was prepared in a dry atmosphere.)

Discussion

The ligands $\underline{o}$-, $\underline{m}$-, and $\underline{p}$-XYNmim were synthesized in the hope of providing environments for copper(I) that would offer some of the stability given by CHXNbim (Chapter 3), at least with respect to disproportionation, but allow greater reactivity. The synthetic methods are more involved than the carboxylic acid-benzimidazole synthesis. However, they can be applied in cases where appropriate starting materials for a benzimidazole synthesis are not readily available, and more than that, give a route to ligands containing imidazole itself or substituted imidazoles. The use of $\underline{N}$-alkylated imidazoles in the present ligands was desired primarily to avoid interference from acidic protons in oxygen reactions. In addition, the 1-methyl-2-imidazolecarboxaldehyde starting material is easier to synthesize than the unmethylated parent compound, and the methyl group provides a useful NMR probe. It is worth mentioning that imidazole compounds

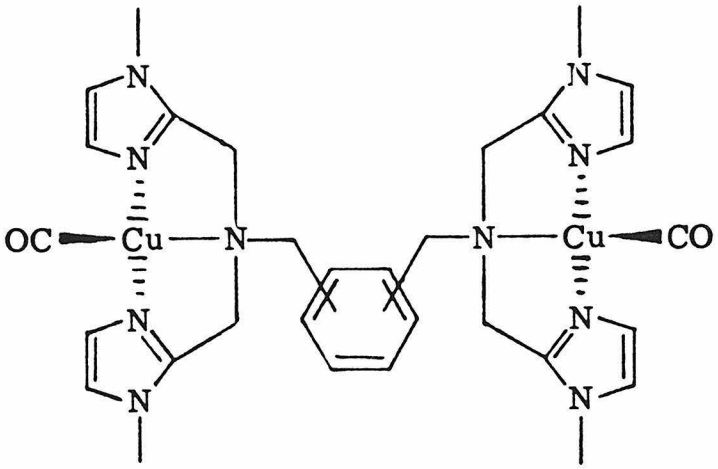
may possess one synthetic advantage over similar materials containing pyridine or pyrazole, in that the former seem to have a greater tendency to form crystalline solids, which simplifies their purification.[18]

The desire to form stable but reactive complexes has been realized. The fact that the complexes do not disproportionate confirms the ability of imidazole to stabilize low coordination numbers of copper(I). The inability of the meta- and para-xylyl ligands to form hexadentate chelates with single copper(II) ions may also be a factor in preventing disproportionation (by destabilizing the disproportionation products). However, the copper(I) complex of the ortho-xylyl ligand does not disproportionate either, although hexadentate chelation probably could occur with this ligand.

As stated previously, the copper(I) complexes of the xylyl ligands are probably all two- or three-coordinate in the solid state. Beyond that, their structures are open to question. The similar complexes containing pyridine and pyrazole groups that have been mentioned (see complexes $\underset{\frown}{2}$ and $\underset{\frown}{3}$ below) have been analyzed crystallographically.[1,2] Both were found to have structures in which each copper ion is coordinated between two nitrogenous heterocycles on the same arm of the m-xylyl bridge, with a third, longer bond to the tertiary amine nitrogen. This gives an approximately T-shaped coordination geometry. However, in these complexes there is an extra methylene group in the chain connecting each heterocycle to the rest of the ligand, which is not present in the $Cu_2(XYNmim)^{2+}$ complexes. Consequently, such coordination would be less favorable in the latter complexes, as it would require the formation of two adjacent five-membered chelate rings in

roughly the same plane and also force a short bond between copper(I) and the "hard" tertiary nitrogen. A short link to the imidazole groups of the XYNmim ligands was chosen, in part, on the rationale that restraining the metal ions to a tetrahedral geometry might help to stabilize an oxygen adduct.

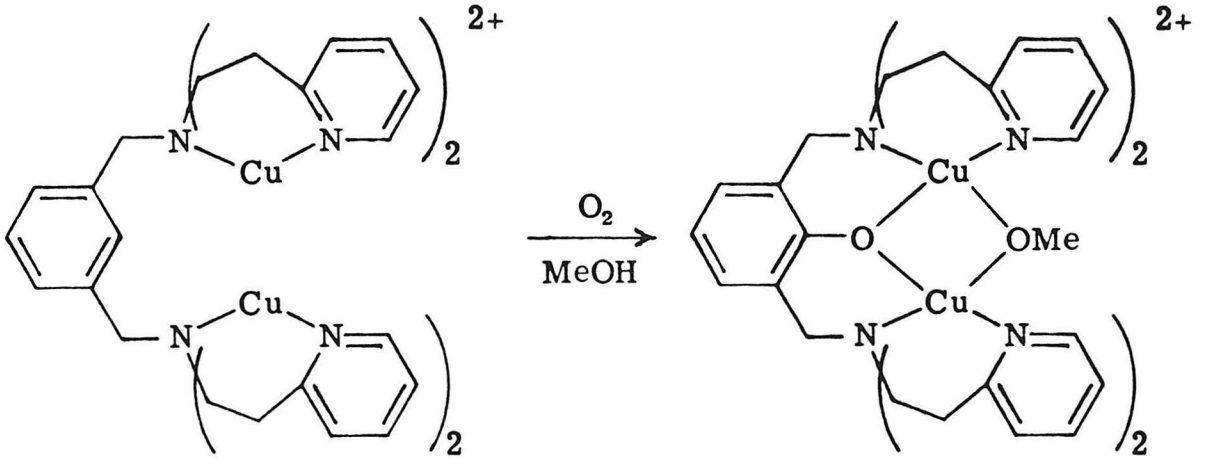
Coordination similar to that found for $Cu_2(TPEN)(BF_4)_2$ (Chapter 2) or its tetrabenzimidazole analogue[17, 19] is a possibility for $Cu_2(\underline{o}\text{-XYNmim})(BF_4)_2$. That is, each copper ion could be bound between imidazole rings attached to different arms of the xylyl group, with or without coordination to an amine nitrogen. Models suggest that such coordination would be much less likely for $Cu_2(\underline{m}\text{-XYNmim})^{2+}$ and impossible for $Cu_2(\underline{p}\text{-XYNmim})^{2+}$. Stable two- or three-coordination might be achieved in these complexes by the formation of dimers or polymers.[20] Whatever the solid-state structures of the complexes are, it seems likely that, as in $Cu_2(TPEN)^{2+}$, the copper ions adopt a pseudotetrahedral geometry upon binding carbon monoxide (structure $\underset{\sim}{1}$).

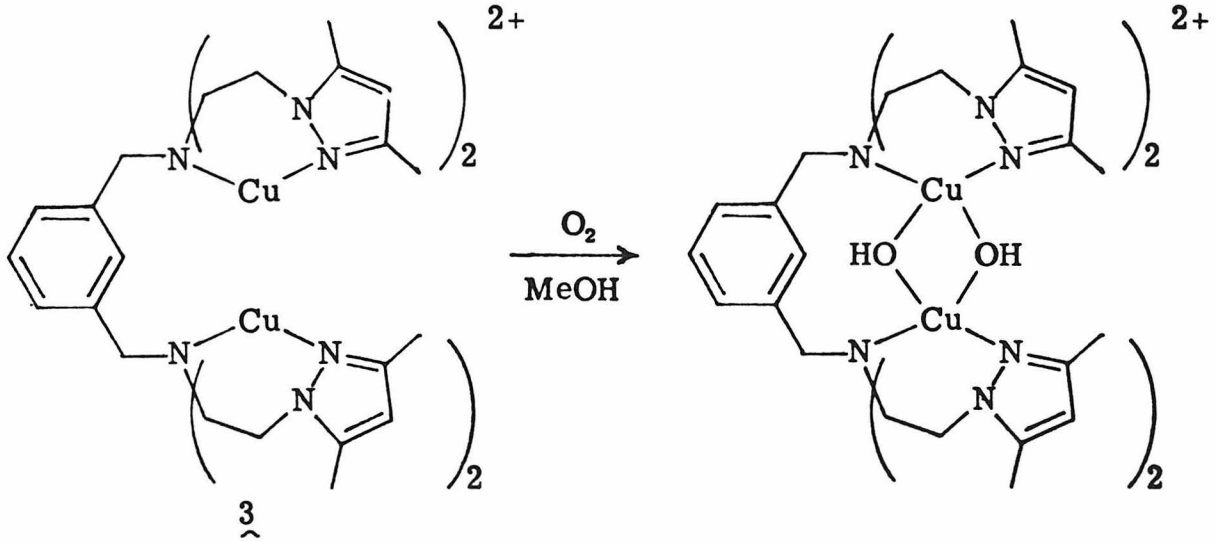


$\underset{\sim}{1}$

The oxygen reactivity of the complexes has turned out to be of relatively little interest. The ortho-xylyl complex shows more complicated behavior than the other two, but since the reaction stoichiometry is 0.25 O_2/Cu at both low and high temperatures, the reasons for this have not been pursued.

It would be of interest to know the reasons for the difference in reactivity of Cu_2(m-XYNmim)$(BF_4)_2$ and complex 2, whose oxygen





reaction might be considered a model for the monooxygenase activity of tyrosinase. The product shown was characterized crystallographically.[3] (Reaction in solvents other than methanol yields a product with a hydroxy rather than a methoxy bridge.[2,3]) On the other hand, the reaction of Cu_2(m-XYNmim)$(BF_4)_2$, like that of complex 3, [1,23] results in oxidation of copper(I) to copper(II) without affecting the ligand. Of course, in the case of Cu_2(m-XYNmim)$^{2+}$ the shorter link between the imidazole ring and the tertiary nitrogen could be a factor in creating the reactivity difference from 2. It might be interesting to prepare a complex in which this link is extended (or possibly a version of 2 in which it is shortened) in order to examine this question. Beyond this, however, are the electronic differences among the three types of heterocycles. Compared to imidazole and pyrazole, pyridine is intermediate in basicity, so the reactivity differences would not seem to be attributable solely to the σ-donor strength of the ligands (pK_a's of the conjugate acids are 7.0, 5.2, and 2.5 for imidazole, pyridine, and pyrazole, respectively[24]). With regard to π properties, imidazole and pyrazole are "π-excessive" heterocycles because they contain a pyrrole nitrogen which donates electrons to the π system. Because pyridine lacks this feature, it is generally regarded as a better π-acceptor ligand.[25] This suggests that π-electronic factors might be important in the oxygen reaction of 2.

Experimental Section

Materials. All chemicals were reagent grade and were used as received unless otherwise noted. Reagent grade dimethylsulfoxide (DMSO) was dried over 4A molecular sieves which had been activated by heating in vacuo at 300°C for several hours. Reagent grade N,N-dimethylformamide (DMF) for oxygen reactions and infrared spectra was dried over activated 4A sieves for 48 hours and then vacuum distilled from additional sieves. Acetonitrile and dichloromethane (spectroscopic grade) for vacuum-line oxygen reactions were stored over 4A sieves and calcium hydride, respectively (with the latter shielded from light), and vacuum transferred prior to reaction. 1-Methyl-2-imidazolecarboxaldehyde was prepared by reaction of the lithium derivative of 1-methylimidazole with DMF, according to the published procedure.[26] (Commercial 1.6 M n-butyllithium in hexane was employed in this process.) 1-Methyl-2-aminomethylimidazole dihydrochloride,[27] potassium phthalimide,[28] and tetra(acetonitrile) copper(I) tetrafluoroborate[29] were also prepared according to literature methods.

Bis(1-methylimidazol-2-ylmethyl)amine. To a stirred mixture of 1-methyl-2-aminomethylimidazole dihydrochloride (11.1 g, 60.3 mmole) in methanol (110 ml) was added 25.2 ml (181 mmole) of triethylamine, resulting in dissolution of the solid. This was followed by addition of 6.64 g (60.3 mmole) of 1-methyl-2-imidazolecarboxaldehyde and 0.9 g of 10% palladium-on-carbon catalyst. The mixture was hydrogenated at 1 atm and 25°C; reaction was complete within ca. 5 hr. After filtration through a Büchner funnel to remove the catalyst,

the solvent was removed by rotary evaporation. To the resulting solid was added 55 ml of chloroform and a solution of 5.3 g of sodium hydroxide in 26 ml H_2O. After mixing, the organic phase was separated, and the aqueous phase was extracted with three additional 55 ml portions of chloroform. The combined extracts were dried (sodium sulfate), and the solvent was removed by rotary evaporation. The crude product was recrystallized from ethyl acetate (50 ml) to give 10.5 g (85%) of colorless crystals. ^{1}H NMR ($CDCl_3$ vs. $SiMe_4$) δ 2.57 (bd, 1), 3.58 (s, 6), 3.82 (s, 4), 6.77 (d, 2), 6.87 (d, 2) (relative intensities in parentheses; bd = broad, s = singlet, d = doublet). Anal. ($C_{10}H_{15}N_5$) C, H, N.[30]

N,N,N′,N′-Tetrakis(1-methylimidazol-2-ylmethyl)-α,α'-diamino-m-xylene (m-XYNmim). To a magnetically stirred solution of bis(1-methylimidazol-2-ylmethyl)amine (3.00 g, 14.6 mmole) in DMSO (19.5 ml) was added N,N-diisopropylethylamine (2.83 g, 21.9 mmole), followed by α,α'-dibromo-m-xylene (1.93 g, 7.31 mmole). The flask was stoppered and the mixture stirred for 30 min. Water (50 ml) was then added, followed by 11.5 ml of 1.4 N NaOH and 15 ml of chloroform. After mixing, the organic phase was removed and the aqueous phase was extracted with two more 15 ml portions of chloroform. Most of the DMSO remained in the aqueous phase, and the rest was removed by washing the combined chloroform extracts with three 15 ml portions of water. After removal of the chloroform by rotary evaporation, the crude ligand was recrystallized from ethyl acetate (190 ml). This produced 2.46 g (66%) of colorless crystals. Anal. ($C_{28}H_{36}N_{10}$) C, H, N.

N,N,N′,N′-Tetrakis(1-methylimidazol-2-ylmethyl)-α,α′-diamino-p-xylene (p-XYNmim). This ligand was prepared by a procedure analogous to that used for m-XYNmim, with one deviation. A 38 ml portion of chloroform was used in the first extraction, followed by two 10 ml portions. The product that crystallized from ethyl acetate originally contained solvent of crystallization, but this was removed on drying for several hours in vacuo. Yield: 2.42 g (65%). Anal. ($C_{28}H_{36}N_{10}$) C, H, N.

2-Phthalimidomethylbenzyl Bromide. Potassium phthalimide (10.5 g, 56.8 mmole) was added to a stirred solution of α,α′-dibromo-o-xylene (15.0 g, 56.8 mmole) in DMF (50 ml) over a period of a few minutes. After most of the potassium phthalimide had been added, a white solid precipitated, causing the mixture to become quite thick in consistency. The remaining potassium phthalimide was added, and the mixture became thinner again after continued stirring. During this process the temperature rose to a maximum of 57°C. The mixture was allowed to cool while stirring was continued. After 50 min the mixture was placed under vacuum and evaporated to dryness. The monophthalimide product and unreacted dibromide were extracted from the resulting solid into 275 ml of acetone. The acetone was removed by rotary evaporation; extraction of the remaining solid with 300 ml of hot petroleum ether (35-60) removed the dibromide and left 7.67 g of crude monophthalimide. This was recrystallized from ethyl acetate and dried for 1 hr in vacuo, giving 6.94 g (37%) of final product. ^{1}H NMR ($CDCl_3$ vs. $SiMe_4$) δ 4.77 (s,1), 4.93 (s,1), 7.15-7.45 (m,2), 7.55-7.85 (m,2) (m = multiplet).

N,N,N′,N′-Tetrakis(1-methylimidazol-2-ylmethyl)-α,α′-diamino-o-xylene-water (2/3) (o-XYNmim · 1.5H_2O). To a magnetically stirred solution of bis(1-methylimidazol-2-ylmethyl)amine (2.00 g, 9.74 mmole) in DMSO (13 ml) was added N,N-diisopropylethylamine (1.89 g, 14.6 mmole) and the monophthalimide described above (3.22 g, 9.74 mmole). The flask was stoppered and the mixture stirred for 45 min. Chloroform (10 ml) was then added, followed by water (32 ml) and 8.00 ml of 1.40 N sodium hydroxide. After mixing, the phases were separated and the aqueous phase was extracted with two more 10 ml portions of chloroform. The combined chloroform extracts were washed with three 10 ml portions of water and then evaporated to dryness, leaving 3.1 g of an amorphous solid. This was dissolved in ethanol (40 ml), hydrazine hydrate (0.360 ml) was added, and the solution was refluxed for 3 hr under nitrogen. At this point 12N HCl (3.4 ml) was added to the hot solution, causing it to become quite dark. The mixture was allowed to cool to room temperature and was then suction filtered to remove the phthalhydrazide that had precipitated. After removal of the solvent by rotary evaporation, the remaining dark oil was dissolved in water (4.5 ml). Addition of 5.5 ml of 5.1N sodium hydroxide caused a dark oil to separate. This mixture was extracted with three 10 ml portions of chloroform, and the combined extracts were dried over sodium sulfate, filtered, and evaporated. After several unsuccessful attempts to purify the resulting material, the synthesis was continued. The crude primary amine (1.55 g) was dissolved in methanol (20 ml) and 1-methyl-2-imidazolecarboxaldehyde (1.11 g) was added. After addition of 10% Pd/C catalyst (0.12 g), hydrogenation was

begun at 1 atm and 50°C. Because the hydrogenation was proceeding slowly, the reaction was interrupted after about 1 hr, the solution was filtered, and hydrogenation was continued after the addition of fresh catalyst. This did little to improve the rate, however. The reaction appeared to be complete after ca. 20 hr. After filtration of the solution the solvent was removed by rotary evaporation, leaving an orange oil. Two recrystallizations of this material from acetone (ca. 60 ml) gave 1.09 g of colorless crystals of o-XYNmim · $1.5H_2O$ (dried in vacuo for 30 min.). A second crop (0.40 g) of less pure material was also obtained, giving a total overall yield of 28%. Anal. ($C_{28}H_{39}N_{10}O_{1.5}$) C, H, N.

Cu_2(m-XYNmim)$(BF_4)_2$. The synthesis of this material was performed under helium in a Vacuum Atmospheres Dri-Lab inert atmosphere chamber. A solution of $Cu(CH_3CN)_4BF_4$ (0.736 g, 2.34 mmole) in methanol (15 ml) was added dropwise, with stirring, to a solution of m-XYNmim (0.600 g, 1.17 mmole) in methanol (ca. 5 ml). White solid began to precipitate after about half of the copper solution had been added. Stirring was continued for 15 min after completion of the addition. The resulting microcrystalline material was collected on a frit by suction filtration, washed with methanol, and dried for 30 min in vacuo. Yield: 0.92 g (96%). Anal. ($C_{28}H_{36}B_2Cu_2F_8N_{10}$) C, H, N, Cu.

Cu_2(o-XYNmim)$(BF_4)_2$ and Cu_2(p-XYNmim)$(BF_4)_2$ were prepared by analogous procedures. The synthesis of the former complex was conducted on two-thirds the scale, and stirring was continued for only 8 min following completion of the addition because of slight evidence of disproportionation. The yield of this complex

(83%) was lower than for the other two. Anal. ($C_{28}H_{36}B_2Cu_2F_8N_{10}$) C, H, N, Cu.

Physical Measurements. Samples of the copper(I) complexes for physical studies were prepared under helium in a Vacuum Atmospheres Dri-Lab inert atmosphere chamber.

Proton magnetic resonance spectra were recorded on a Varian EM-390 spectrophotometer at 90 MHz (34°C). CD_3CN was used as the solvent for the complexes and $CDCl_3$ for most organic materials, with $SiMe_4$ as an internal reference in either case.

Infrared spectra were recorded on a Beckman IR 4240 spectrophotometer. Solid-state samples were prepared as Nujol mulls, pressed between KBr plates. Samples of the complexes for solution spectra under CO were first dissolved in DMF under helium. Each solution was then saturated with CO and transferred via a cannula to a solution cell (CaF_2, 1mm path) sealed with septum caps.

Electronic spectra were recorded on a Cary 14 spectrophotometer. Elemental analyses were performed by the Caltech Microanalytical Laboratory or Galbraith Laboratories, Inc..

Oxygen Uptake Measurements. In each experiment a sample of copper(I) complex (ca. 0.07 mmole) was placed in a vial under helium, then transferred to a preweighed 10 ml round-bottom flask in air and rapidly weighed on an analytical balance. A magnetic stir bar was then added to the flask, which was quickly connected to an 8 ml calibrated

volume apparatus on a vacuum line and evacuated. (Samples usually acquired a very slight bluish coloration during this procedure. One experiment with Cu_2(m-XYNmim)$(BF_4)_2$ was repeated using a procedure in which all transfers of the solid were conducted under helium, but this had no significant effect on the results.) Solvent (ca. 5 ml) was vacuum transferred to the flask, which was then closed from the rest of the apparatus. The calibrated volume was filled with a measured pressure of oxygen (ca. 400 Torr), the temperature was noted, and the calibrated volume was closed off. For low-temperature reactions the sample flask was immersed in an ethanol/water slush bath kept at $-30 \pm 2^{\circ}C$. The flask was then opened to the calibrated volume and the solution was stirred for 45 min. At the end of this period the solution was frozen in liquid nitrogen and the oxygen that remained was collected by means of a Toepler pump, after passing through two liquid nitrogen traps. The reaction solution was completely degassed after three freeze-pump-thaw cycles. The pressure and temperature of the oxygen, which had been collected into a calibrated volume (14.00 ml), were noted, and the quantity consumed was calculated by difference.

Samples of the Cu_2(m-XYNmim)$(BF_4)_2$ oxygen reaction product, obtained from acetonitrile or DMF solutions after removal of the solvent under vacuum, could be recrystallized from acetonitrile/methanol. This was done by dissolving the material in a small amount of acetonitrile, evaporating the solution to a blue oil under reduced pressure,

and adding methanol. Various samples obtained in this way appeared to be identical from their infrared spectra; one gave an elemental analysis consistent with the formula $C_{29}H_{41}B_2Cu_2F_8N_{10}O_{2.5}$. Calcd: C, 40.02; H, 4.75; N, 16.09. Found: C, 39.98; H, 4.74; N, 15.94.

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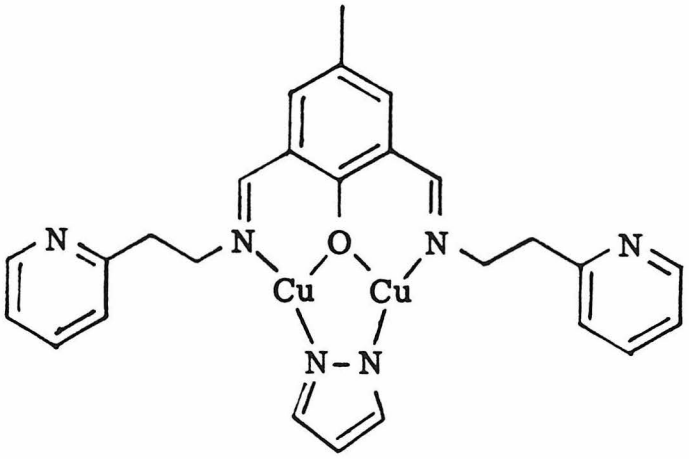
CHAPTER 5

Summary and Conclusions

A series of complexes have been presented which contain two copper(I) ions bound to various types of nitrogenous bases. In each case each copper ion appears to be coordinated to only two or three nitrogen atoms. Recent evidence indicates that this statement also applies to the active site of deoxyhemocyanin.[1,2] X-ray structural analysis of two of the complexes described in this thesis (1, which also contains an oxygen ligand, and 2) have shown that this type of coordination can sometimes foster direct copper-copper interaction. This does not appear to be the case in deoxyhemocyanin, however.[1,2]

The studies that have been presented have shown that changes in the coordination environment of copper(I), some of which, a priori,



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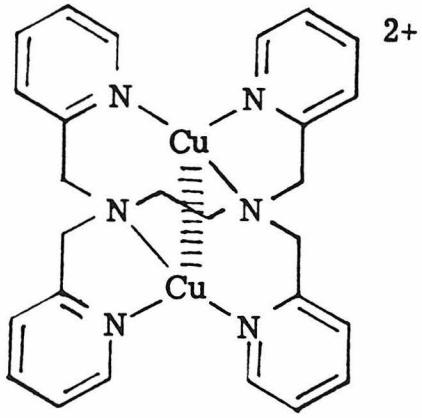

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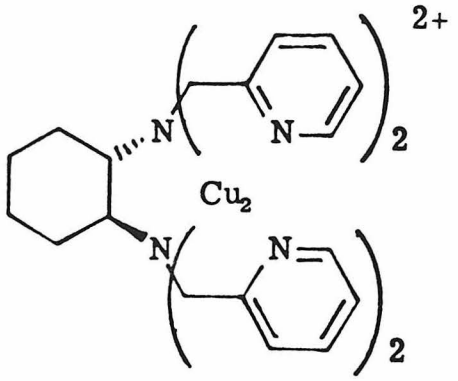

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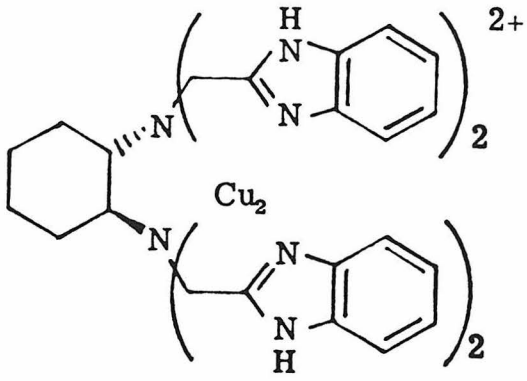
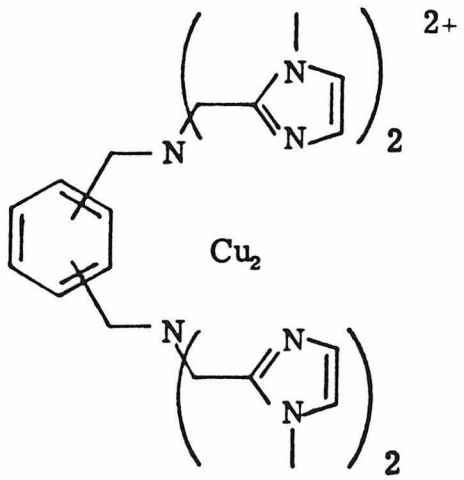


4

might seem relatively minor, can produce widely varying stability and reactivity. Complexes 2 and 3 disproportionate in solution (in the absence of other ligands), whereas 1 and 4 through 7 do not. Although the copper ions in all of the complexes are only two- or three-coordinate (excluding metal-metal interactions), only 2, 3, and 5-7 form adducts with additional ligands such as carbon monoxide. Both of the copper ions of 1 appear to have open coordination sites in solution as

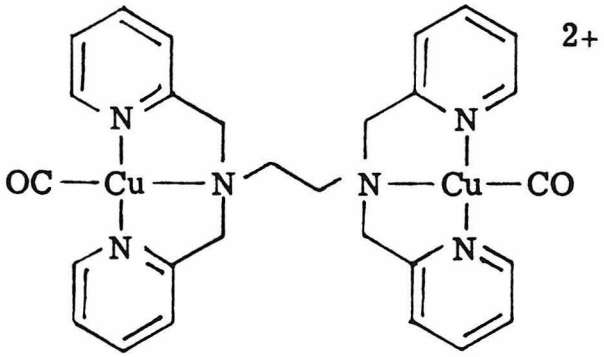
5 o-xylyl
6 m-xylyl
7 p-xylyl



well as the solid state, but nevertheless do not bind carbon monoxide. Complex 4 does not react with CO and reacts only slowly with oxygen.

Compound 2 has been shown to undergo major structural rearrangement on binding carbon monoxide, to give 8. The formation of this adduct resembles the oxygenation of hemocyanin in this respect, since the latter also appears to involve significant changes in coordination at the active site, other than the binding of dioxygen.[1,3] (The oxygenation of hemocyanin also involves an increase in the oxidation state of copper, however.) Presumably the other complexes which bind carbon monoxide (3, 5, 6, and 7) also yield structures similar to 8.

Understanding the reasons for the varying reactivity of the above complexes with carbon monoxide would be helpful in explaining the reactivity of the hemocyanin active site. Deoxyhemocyanin forms a carbonyl adduct, but with a stoichiometry of one molecule of CO per two copper ions.[4-6] Since the C-O stretching frequency (~2060 cm^{-1}) is indicative of a terminal carbonyl, one of the metals evidently does not bind CO. This might be attributable to some of the same factors that



8

control the reactivity of 1 and 4.

One factor that probably contributes to the stability of 1 and 4, and likely 5-7 as well, is linear coordination of copper between two nitrogen ligands which are not particularly good π-acceptors. This appears to stabilize copper(I) with respect to disproportionation, and also, at least under some circumstances, seems to have a prohibitive effect on the binding of additional ligands. Pyridine, which is a better π-acid than imidazole, pyrazole, or the imine functionality, promotes higher coordination numbers. (A larger number of ligands might be expected to stabilize a larger number of filled metal d orbitals as a consequence of mixing with empty ligand π orbitals.[7]) Lack of a sufficient number of ligands appears to be the reason for metal-metal interaction and lack of stability with respect to disproportionation in complex 2 and probably also 3.

Steric effects which inhibit the rearrangement of two- or three-coordinate complexes to a tetrahedral geometry undoubtedly contribute to low reactivity. Such effects likely operate in complex 4 in addition to electronic effects. However, this still does not seem to explain entirely the lack of reactivity of 1 toward additional ligands such as CO. Further research would be desirable to gain a more complete understanding of these phenomena and enable better prediction of the reactivity of coordinatively unsaturated copper(I) complexes.

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APPENDIX

Unusual Structural and Reactivity Types for Copper(I): Synthesis, Structural and Redox Properties of Binuclear Copper(I) Complexes which are Probably Three-Coordinate in Solution and Experience Intermolecular Metal-Metal Interactions in the Solid State.

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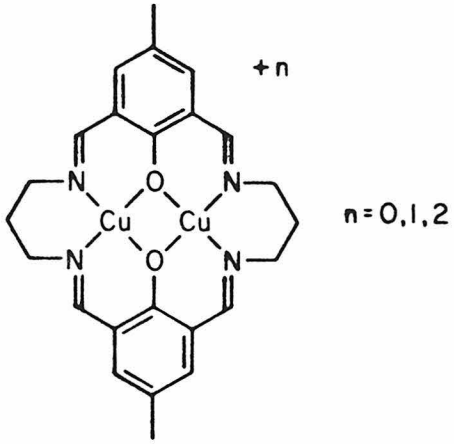
Contribution No. 5645 from the Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125.

Introduction

Protein binuclear copper sites effect remarkable reactions with dioxygen including reversible binding (hemocyanin),[1] activation (tyrosinase)[2] and reduction (laccase).[3] Structural information contrasting these active sites is limited but similarities are notable: sulfur ligands have been proposed but most studies suggest only nitrogen and/or oxygen coordination;[4] in the oxidized forms all three binuclear sites are strongly antiferromagnetically coupled;[5,6] the tyrosinase and laccase binuclear sites exhibit two electron reductions at potentials which are rather high for the proposed all nitrogen/oxygen copper coordination.[6,7]

Model studies have addressed ligand environment(s), redox properties, magnetic interactions and dioxygen binding in these protein active sites.[8-12] To help define protein structure/reactivity relationships we are endeavouring to catalogue fundamental copper(I) coordination chemistry in relatively simple mononuclear and binuclear complexes. As discussed elsewhere, polydentate ligands, including macrocycles, can be utilized to minimize problems associated with both copper(II) and copper(I) substitution lability.[13,14] This approach has resulted in unusual structural and reactivity types for copper including four- and five-coordinate copper(I) species.[13-15] The binuclear complex $\underset{\sim}{1}$ provided an opportunity for measuring intramolecular electron transfer rates between copper centers, but the reduction potentials observed for $\underset{\sim}{1}$ (equations 1 and 2) are significantly more negative than those exhibited by the proteins (e.g., +0.36 V for

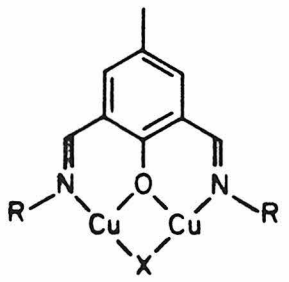


1

$$Cu^{II}Cu^{II}L^{2+} + e^- \underset{}{\overset{-0.52\,V}{\rightleftharpoons}} Cu^{II}Cu^{I}L^{+} \qquad (1)$$

$$Cu^{II}Cu^{I}L^{+} + e^- \underset{}{\overset{-0.91\,V}{\rightleftharpoons}} Cu^{I}Cu^{I}L \ . \qquad (2)$$

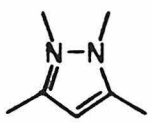
tyrosinase).[7,14] Modification of the macrocyclic complex, 1, has yielded a series of binuclear complexes 2, in which the R and X groups



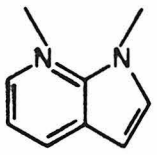
2

X = 

,



,



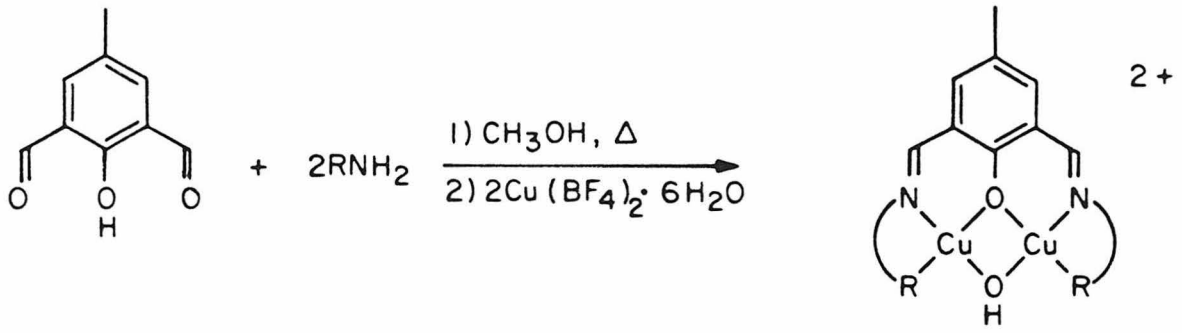
were varied systematically, resulting in a wide range of reduction potentials. In this manner, utilizing only nitrogen and oxygen ligands, high reduction potentials comparable to that of protein binuclear sites have been achieved. The new binuclear copper(I) complexes appear to be only three-coordinate in solution but in some instances experience significant intermolecular copper(I)-copper(I) interactions in the solid state.

Synthesis and Characterization of Complexes

Three copper(II) complexes, 3-5, were prepared by simple condensation of 2-hydroxy-5-methylisophthalaldehyde with primary amines followed by addition of copper(II), Scheme I. The new compounds are blue-green due to weak absorption in the 630-645 nm region (probably ligand field transitions) as listed in Scheme I for methanol solutions. Solid state magnetic susceptibility measurements at 25° C, also listed in Scheme I, suggest that the two copper(II) centers are antiferromagnetically coupled.

Analogous air sensitive copper(I) complexes were prepared in a helium atmosphere in a fashion similar to the synthesis of the copper(II) species. The dialdehyde was condensed with two equivalents of a primary amine, RNH_2, then treated with a bridging bidentate ligand, XH, in the presence of base, followed by addition of $Cu(CH_3CN)_4BF_4$ (Scheme II). The compounds synthesized, along with the abbreviations to be used, are listed in Table I. All of the compounds listed gave satisfactory C, H and N analyses. Selected compounds were also analyzed for copper, giving the expected values. The infrared spectra

Scheme I. Preparation of Binuclear $Cu^{II}Cu^{II}$ Complexes. (Spectra were recorded in methanol solution at 25° C. Magnetic susceptibilities are given in B.M., measured at 25° C, and corrected for diamagnetism, but not for T.I.P.)



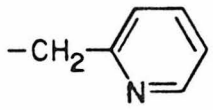
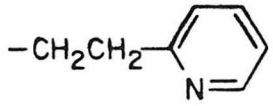
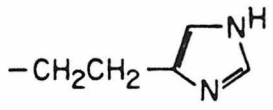
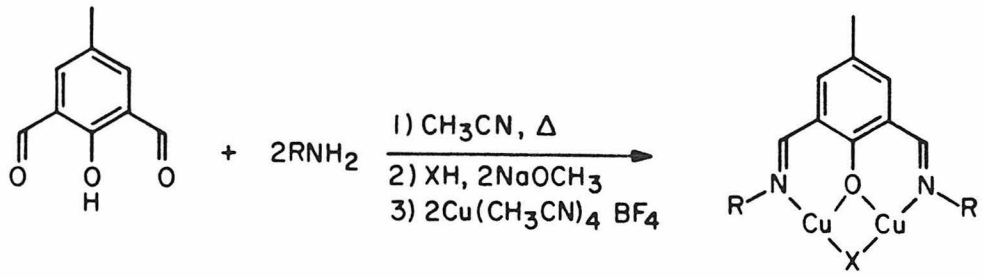
	R	λ (ε)	μ_{eff}/Cu
3		630(160)	1.4
4		645(120)	1.2
5		630(100)	0.96

Table I. Binuclear Cu(I)-Cu(I) Complexes, Abbreviations Utilized and NMR Data.

Compound Number	Sidearm (R)	Bridge (X)	Abbreviation	NMR Assignments[a] α_1	α_2	α_3	β_1	β_2	py_1	pz_2	pz_3	aza_2	aza_3	aza_6
6	2-(pyridyl)-methyl	pyrazolate	$Cu(I)_2ISOIM(Mepy)_2(pz)$	2.05	6.66	7.56	4.60	-	8.46	8.02	6.23	-	-	-
7	2-(pyridyl)-methyl	3-5 dimethyl-pyrazolate	$Cu(I)_2ISOIM(Mepy)_2(Me_2pz)$	2.06,s	6.69,s	7.72,s	4.67,s	-	8.37,d	2.13,s/b	6.21	-	-	-
8	2-(pyridyl)-methyl	7-azaindolate	$Cu(I)_2ISOIM(Mepy)_2(aza)$	2.09,s	6.72	7.54	4.70,s	-	8.43,d	-	-	c	c	c
9	2-(2'-pyridyl)-ethyl	pyrazolate	$Cu(I)_2ISOIM(Etpy)_2(pz)$	1.92,s	6.47	7.50	3.82,t	3.29,t	8.42,d	7.87	6.47	-	-	-
10	2-(2'-pyridyl)-ethyl	3-5 dimethyl-pyrazolate	$Cu(I)_2ISOIM(Etpy)_2(Me_2pz)$	1.94,s	6.48,s	7.52,s	3.88,t	3.37,t	8.40,d	2.46,s/b	6.17	-	-	-
11	2-(2'-pyridyl)-ethyl	7-azaindolate	$Cu(I)_2ISOIM(Etpy)_2(aza)$	1.96,s	c	7.60	3.90,t	3.44, 3.20	8.39	-	-	8.10	c	8.39
12	phenylmethyl	pyrazolate	$Cu(I)_2ISOIM(MePh)_2(pz)$	2.10,s	6.72	7.54	4.26	-	-	8.00	6.26	-	-	-
13	phenylmethyl	3-5 dimethyl-pyrazolate	$Cu(I)_2ISOIM(MePh)_2(Me_2pz)$	2.10,s	6.70	7.57	4.37	-	-	2.06,s/b	c	-	-	-
14	phenylmethyl	7-azaindolate	$Cu(I)_2ISOIM(MePh)_2(aza)$	2.14,s	6.77	c	4.40, 4.32	-	-	-	-	c	c	c
15	2-phenylethyl	pyrazolate	$Cu(I)_2ISOIM(EtPh)_2(pz)$	1.96,s	6.51	7.37	3.45,t	3.07,t	-	7.93,d	6.51	-	-	-
16	2-phenylethyl	3-5 dimethyl-pyrazolate	$Cu(I)_2ISOIM(EtPh)_2(Me_2pz)$	1.97,s	6.52,s	7.38,s	3.50,t	3.10,t	-	2.61,s/b	6.17	-	-	-
17	2-phenylethyl	7-azaindolate	$Cu(I)_2ISOIM(EtPh)_2(aza)$	1.98,s	6.53,s	7.46,s	3.52,t	3.18, 2.97	-	-	-	8.13,d	c	8.36,d
18	n-propyl	pyrazolate	$Cu(I)_2ISOIM(1\text{-}Pr)_2(pz)$	2.09,s	6.70,s	7.57,s	3.15,t	1.78,m	-	7.87,d	6.43,t	-	-	-
19	i-propyl	pyrazolate	$Cu(I)_2ISOIM(2\text{-}Pr)_2(pz)$	2.10,s	6.70,s	7.70,s	2.90,m	1.20,d	-	7.87,d	6.45,t	-	-	-
20	t-butyl	pyrazolate	$Cu(I)_2ISOIM(t\text{-}Bu)_2(pz)$	2.13,s	6.85,s	7.91,s	-	1.26,s	-	7.93,d	6.54,t	-	-	-
21	t-butyl	3-5 dimethyl-pyrazolate	$Cu(I)_2ISOIM(t\text{-}Bu)_2(Me_2pz)$	2.10,s	6.81,s	7.85,s	-	1.28,s	-	2.57,s/b	6.10,s	-	-	-
22	t-butyl	7-azaindolate	$Cu(I)_2ISOIM(t\text{-}Bu)_2(aza)$	2.14,s	6.85,s	7.98,s	-	1.34,s 1.23,s	-	-	-	8.13,d	6.75,d	8.45,d
23	phenyl	pyrazolate	$Cu(I)_2ISOIM(Ph)_2(pz)$	2.04,s	6.67	7.52	-	-	-	7.75,d	6.33	-	-	-
24	p-(dimethylamino)-phenyl	pyrazolate	$Cu(I)_2ISOIM(PhNMe_2)_2(pz)$	2.07	c	7.55	-	-	-	c	c	-	-	-
25	p-acetylphenyl	pyrazolate	$Cu(I)_2ISOIM(PhCOMe)_2(pz)$	c	c	c	-	-	-	c	c	-	-	-

[a]All spectra were obtained in d^6 benzene solution at 34°C. The values listed are given in ppm, δ, relative to TMS. The assignments for the resonances are given in Figure 2 and as follows: α_1 = protons from the methyl group on the aromatic ring arising from 2-hydroxy-5-methylisophthalaldehyde; α_2 = aromatic protons from the 2-hydroxy-5-methyl-isophthalaldehyde ring; α_3 = the imine protons; β_1 = methylene protons (or methine proton) adjacent to the imine nitrogen; β_2 = methylene (or methyl) protons two carbons away from the imine nitrogen; py_1 = the protons on the carbon adjacent to the pyridine nitrogen; pz_2 = protons in the 2 and 4 positions on the pyrazole ring; pz_3 = proton in the 3 position on the pyrazole ring; aza_2, aza_3, aza_6 = the protons on the 2,3 and 6 positions, respectively, on the 7-azaindole bridge. S = singlet, d = doublet, t = triplet, m = multiplet. If not listed in the Table, the multiplicity could not be determined due to broadness or overlapping of the peaks. [b]These peaks are assigned to the methyl groups attached to the pyrazole ring. [c]These peaks could not be discerned because of overlapping peaks and/or limited solubility.

Scheme II.



of all compounds showed the absence of aldehydic carbonyl and amine N-H stretches, consistent with complete imine condensation. The multitude of peaks in the region 700 - 1640 cm^{-1} made absolute assignments difficult.

Mass spectra were obtained for compounds 16, 19, 20, 21, and 22, each of which exhibits parent ion peaks in agreement with the formulation given above. The presence of two coppers in these compounds is indicated by three parent peaks due to the presence of both ^{63}Cu and ^{65}Cu. The relative intensities of these three peaks, averaged over all the compounds analyzed, were 1:0.90:0.24 for $^{63}Cu_2L$:$^{63}Cu^{65}CuL$:$^{65}Cu_2L$ (theoretical ratio is 1:0.89:0.20).

The electronic absorption spectrum of $Cu_2^{I}ISOIM(EtPh)_2(pz)$, 15, shown in Figure 1 (curve B), is typical of the solution spectrum of all the binuclear copper(I) complexes examined. Spectra obtained in the solid state (nujol mulls) varied. The solid state spectrum of $Cu_2^{I}ISOIM(EtPh)_2(pz)$, 15, shown in Figure 1 (curve A), is typical of

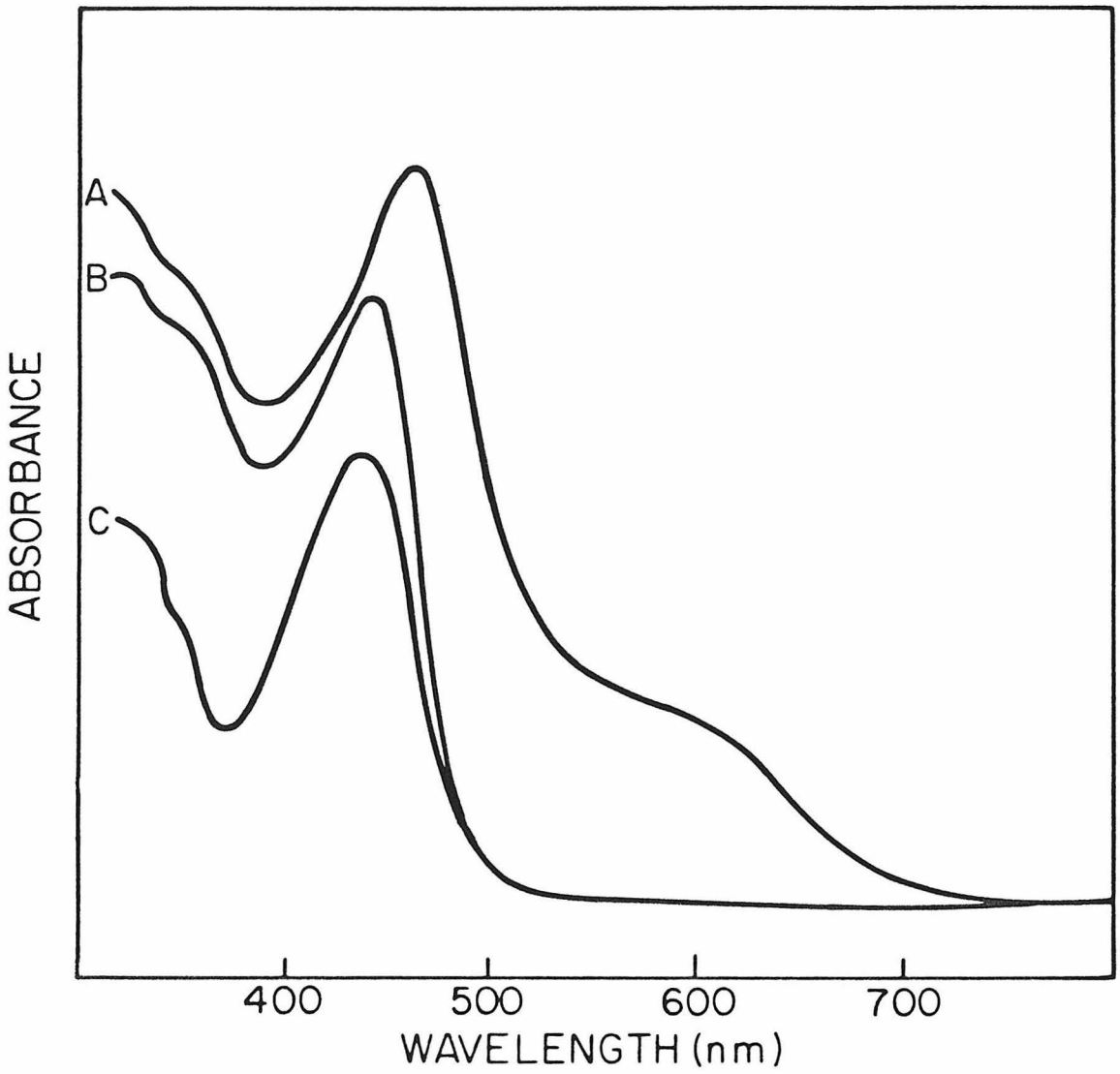


Figure 1. Electronic absorption spectra: (A), Cu^{I}_{2}ISOIM(EtPh)$_2$(pz), 15, in the solid state; (B), Cu^{I}_{2}ISOIM(EtPh)$_2$(pz), 15, in a hexane solution; and (C), Cu^{I}_{2}ISOIM(t-Bu)$_2$(pz), 20, in the solid state.

that for most compounds examined. Note that the absorption present in solution at 444 nm (ϵ = 8600) shifts to lower energies, ca. 464 nm, in the solid state. In addition a new absorption was found in the solid state spectrum at ca. 600 nm. The 600 nm absorption was not found in solution even in spectra of concentrated THF solutions, in which these compounds are considerably soluble.

Not all species examined exhibit the solid state spectrum described above. Compounds 19, 20, 21, and 22 exhibit solid state spectra as shown for Cu_2^{I}ISOIM(t-Bu)$_2$(pz), 20, in Figure 1 (curve C), which can be compared to the solution spectra of all complexes. Under no conditions have compounds 19-22 shown notable absorption in the 600 nm region.

All cuprous compounds were shown to be diamagnetic by the presence of very sharp NMR resonances (see Figure 2). Table I lists the peaks observed for each complex. The assignments given were made by cross-comparisons of all the spectra. In each case, the identity of the organic entity is confirmed. Integration values were in agreement with the proposed structures.

Solution Reactivity. All compounds presented here are unreactive towards carbon monoxide. This was shown definitively for CO saturated solutions (CH_2Cl_2) of Cu_2^{I}ISOIM(Etpy)$_2$(pz), 9, and Cu_2^{I}ISOIM(1-Pr)$_2$(pz), 18, both of which show infrared absorptions in the region 1500-1650 cm^{-1}, characteristic of the original complex, 9 or 18, but neither shows any bands in the region 1700-2200 cm^{-1} which would be attributable to a carbonyl complex. Also, evaporation of THF solutions of these compounds with a stream of CO gave the original compounds, as identified

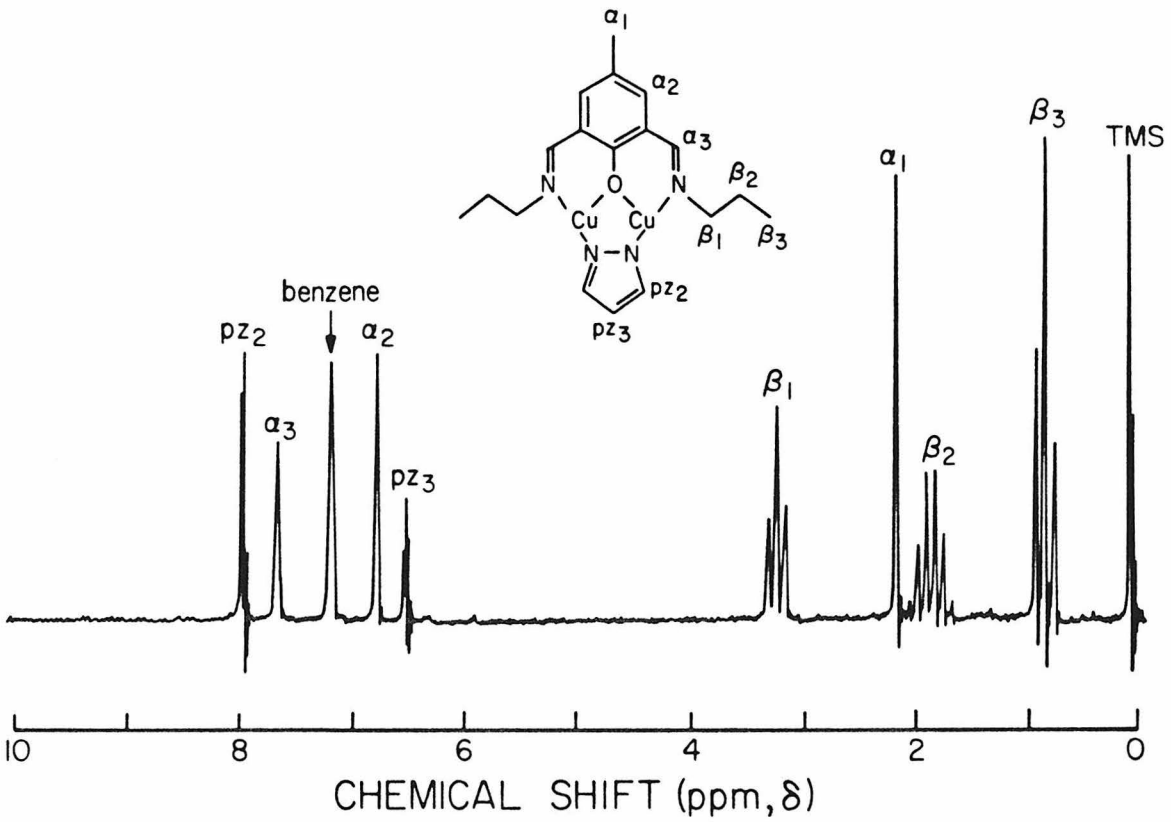


Figure 2. NMR spectrum of Cu^{I}_{2}ISOIM(1-Pr)$_2$(pz), 18, in d^6 benzene at 34° C.

by IR spectra.

All copper(I) compounds react with oxygen at the ambient temperature to form green or brown products from orange DMF solutions. This reaction could not be reversed by subsequent bubbling of argon through the solutions. The air sensitivity of these complexes prevented reliable solution molecular weight measurements.

Electrochemistry. All electrochemical results presented here were obtained in DMF solutions at a platinum indicating electrode. Ferrocene was used as an internal standard and all potentials have been converted to versus nhe using E^f = +0.40 mV vs. nhe for ferrocene.[16] The cyclic voltammograms for the Cu(II) compounds, 3-5, were irreversible as shown in Figure 3 for $Cu_2^{II}ISOIM(Mepy)_2(OH)^{2+}$, 3. Addition of one equivalent of pyrazole to the same solution, however, gave the quasi-reversible electrochemistry also shown in Figure 3.[17] Similar results were observed for $Cu_2^{I}ISOIM(Etpy)_2(OH)^{2+}$, 4. In contrast $Cu_2^{I}ISOIM(hist)_2(OH)^{2+}$, 5, gave very irreversible electrochemistry even with added pyrazole.

Constant potential electrolysis (cpe) of 3 plus an equivalent amount of pyrazole at -0.35 V and -0.70 V indicated that each wave corresponds to a one-electron process. No attempt was made to isolate a mixed valence species, but the binuclear cuprous complex, $Cu_2^{I}ISOIM(Mepy)_2(pz)$, 6, was synthesized by cpe of an acetonitrile solution containing $Cu_2^{II}ISOIM(Mepy)_2(OH)^{2+}$, 3, and an equivalent amount of pyrazole at -0.70 V (n = 2.0).

The cyclic voltammogram for $Cu_2^{I}ISOIM(Mepy)_2(pz)$, 6, was, of course, identical to that shown in Figure 3 for 3 plus one equivalent

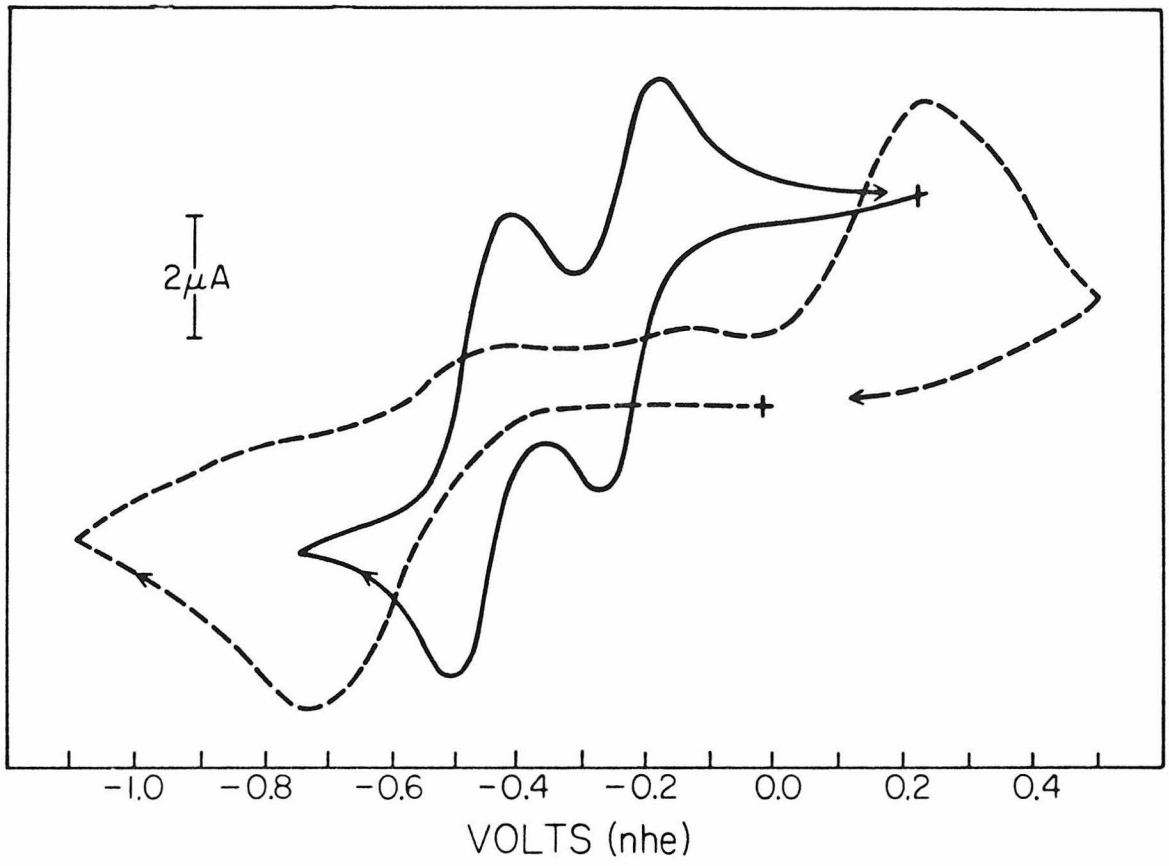


Figure 3. Cyclic voltammograms of DMF solutions: Cu^{II}_2-ISOIM(Mepy)$_2$(OH)$^{2+}$, 3, (----); Cu^{II}_2ISOIM(Mepy)$_2$(OH)$^{2+}$, 3, containing one equivalent of pyrazole (——). Both voltammograms were observed with a platinum electrode, using 0.1M TBAP as the electrolyte at a scan rate of 200 mV/sec.

of pyrazole. All binuclear copper(I) compounds presented in Table II exhibited cyclic voltammetry similar to the solid line in Figure 3; however, large peak separations (Ep_a-Ep_c = 100-150 mV at 50 mV/sec) were observed for many compounds at a platinum electrode.[18] Cyclic voltammetry at a hanging mercury drop electrode (HMDE) gave smaller peak separations (70-90 mV) for most compounds, and the formal potentials (E^f) were identical to those observed using a platinum electrode. The potentials recorded in Table II were determined at a platinum electrode because this electrode allowed direct comparison with the internal standard, ferrocene, on the same scan. It was found that the potentials could be read more accurately using differential pulse voltammetry, and this technique was employed to obtain the values presented in Table II. In all cases, the formal potentials were within 10 mV of the potentials observed by cyclic voltammetry. All compounds containing the 7-azaindole anion as the bridge exhibited irreversible electrochemistry, often showing two anodic waves but only ill-defined cathodic waves, and hence the electrochemistry of these species is not included here.

Constant potential electrolysis at a potential 200 mV more positive than the second oxidation peak was performed on compounds 6, 9, 10, 19, and 20, as typical Cu(I) species, and each gave a two-electron oxidation (n = 2.0 ± 0.1).

The average separation of the two formal potentials (E_1^f-E_2^f) is 194 ± 40 mV for all new compounds listed in Table II. From this value for E_1^f-E_2^f, the average comproportionation constant, K, is calculated to be 1.9×10^3 for the equilibrium in equation 3, where L represents the entire ligand system.[14] Note that all complexes containing a

Table II. Reduction Potentials for Binuclear Copper Complexes.[a]

$$Cu(II)Cu(II)L^{+2} + e^- \overset{E_1^f}{\rightleftharpoons} Cu(II)Cu(I)L^+$$

$$Cu(II)Cu(I)L^{+2} + e^- \overset{E_2^f}{\rightleftharpoons} Cu(I)Cu(I)L$$

No.	Compound	E_1^f [b]	E_2^f [b]	n[c]
1	$Cu(II)_2(ISOIM)_2(Pr)_2^{+2}$	-0.52[d]	-0.91[d]	-
6	$Cu(I)_2ISOIM(Mepy)_2(pz)$	-0.211	-0.452	2.0
7	$Cu(I)_2ISOIM(Mepy)_2(Me_2pz)$	-0.190	-0.374	-
9	$Cu(I)_2ISOIM(Etpy)_2(pz)$	-0.110	-0.344	2.0
10	$Cu(I)_2ISOIM(Etpy)_2(Me_2pz)$	-0.113	-0.267	2.0
12	$Cu(I)_2ISOIM(MePh)_2(pz)$	0 146	-0.081	-
13	$Cu(I)_2ISOIM(MePh)_2(Me_2pz)$	0.206	0.005	-
15	$Cu(I)_2ISOIM(EtPh)_2(pz)$	0.128	-0.078	-
16	$Cu(I)_2ISOIM(EtPh)_2(Me_2pz)$	0.205	0.009	-
18	$Cu(I)_2ISOIM(1\text{-}Pr)_2(pz)$	0.146	-0.076	-
19	$Cu(I)_2ISOIM(2\text{-}Pr)_2(pz)$	0.193	0.001	1.9
20	$Cu(I)_2ISOIM(t\text{-}Bu)_2(pz)$	0.240	0.053	2.0
21	$Cu(I)_2ISOIM(t\text{-}Bu)_2(Me_2pz)$	0.239	0.080	-
23	$Cu(I)_2ISOIM(Ph)_2(pz)$	0.144	-0.032	-
24	$Cu(I)_2ISOIM(PhNMe_2)_2(pz)$	0.146	-0.048	-
25	$Cu(I)_2ISOIM(PhCOMe)_2(pz)$	0.152	0.008	-

[a] These values were measured by differential pulse polarography in DMF using a platinum indicating electrode. [b] Potentials are given in volts vs. nhe. Potentials were measured vs. ferrocene as an internal redox couple then corrected to vs. nhe using a value of 0.40V for ferrocene vs. nhe. [c] These values for n were determined by constant potential electrolysis at a potential 200 mV more positive than E_1^f. Values are given for all complexes actually examined by cpe. [d] Reference 13.

$$Cu^{I}Cu^{I}L + Cu^{II}Cu^{II}L^{2+} \overset{K}{\rightleftharpoons} 2Cu^{II}Cu^{I}L^{+} \qquad (3)$$

3,5-dimethylpyrazolate bridge have smaller formal potential separations ($E_1^f - E_2^f$) and correspondingly smaller comproportionation constants than their pyrazolate bridged analogues.

Addition of excess pyridine (up to one hundred-fold excess) to the electrochemical solutions of 6, 12, and 13 did not cause a significant shift (< 10 mV) in the potentials, but merely broadened the peaks. Cyclic voltammetry of 6, 7, 9, and 10 in other solvents such as CH_2Cl_2, CH_3CN and THF, gave similar behavior to that observed in DMF, while the electrochemistry for all other compounds was irreversible in these alternative solvents.

Crystallographic Analysis

The crystal and molecular structure of $Cu_2^{I}ISOIM(Etpy)_2(pz)$, 9, was determined. Basic crystal data are summarized in Table III. Tables IV-VII present the atomic parameters and interatomic distances and angles. The atom labeling scheme is illustrated in Figure 4.

The bonds to the copper atoms are shown in Figure 4. Each copper is bound to three ligand atoms in what is almost a tee geometry, the largest angles being 167.6° (N1-Cu1-N3) and 170.7° (N2-Cu2-N4). The intramolecular copper-copper distance, 3.304 Å, is sufficiently long that any direct interaction is unlikely.

There still remains, however, the possibility of direct intermolecular interaction between copper atoms. The molecules form an

Table III. Basic Crystal Data for $Cu(I)_2ISOIM(Etpy)_2(py)$, 9.

$C_{26}H_{26}Cu_2N_6O$

FW = 565.6	V = 2502.3 (10) Å^3
space group $P2_1/c$ (No. 14)	Z = 4
a = 20.980 (4) Å	ρ_{calc} = 1.50 g cm^{-3}
b = 4.929 (1) Å	μ = 23.8 cm^{-1}
c = 24.773 (6) Å	$\lambda(CuK_\alpha)$ = 1.5418 Å
β = 102.38 (2)°	

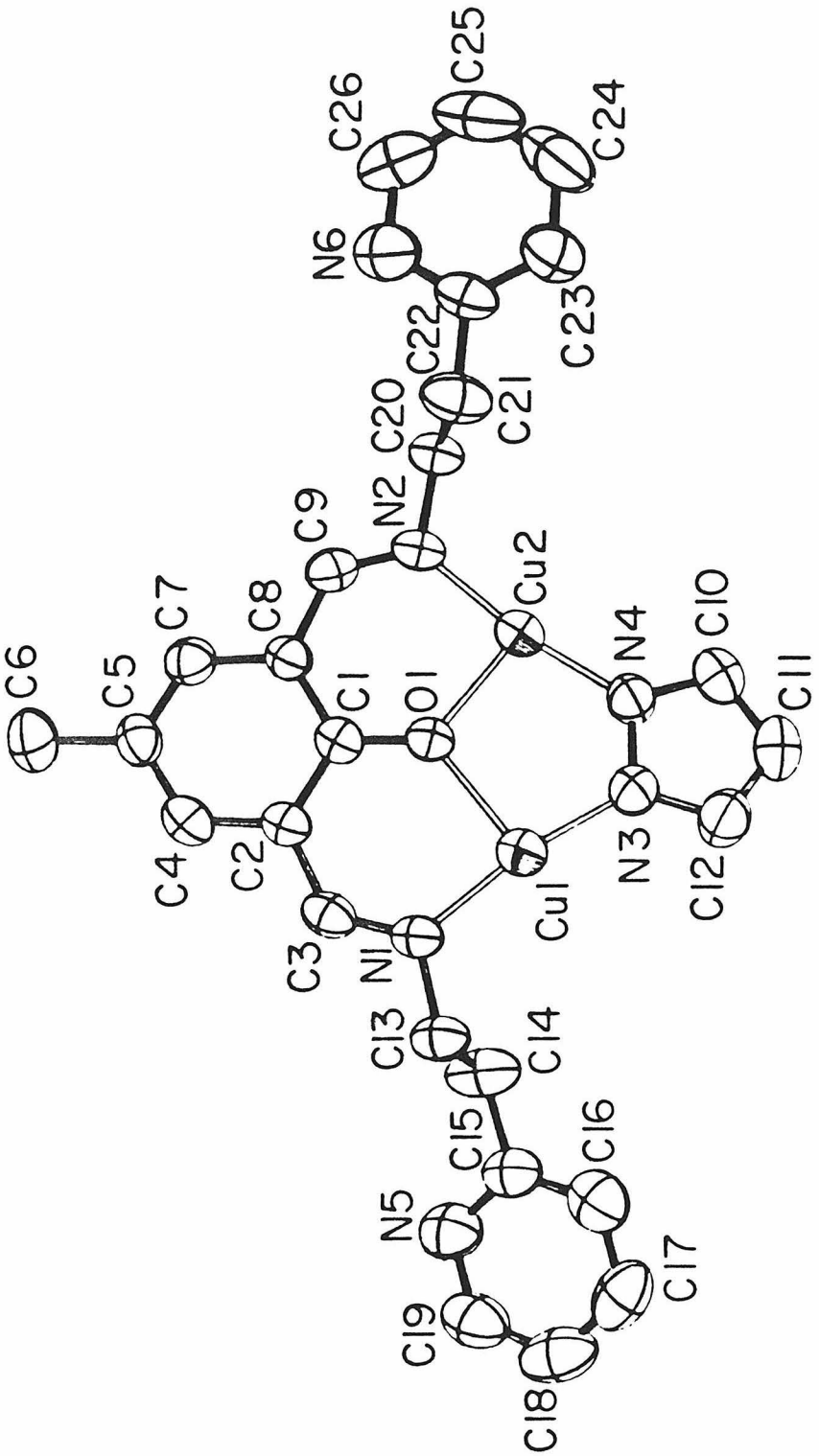


Figure 4. ORTEP drawing of Cu^{I}_{2}ISOIM(Etpy)$_2$(pz), 9, including atomic labeling scheme. Each hydrogen is given the same number as the carbon to which it is bound.

Table IV. Atomic Parameters and ESD's for $Cu(I)_2ISOIM(Etpy)_2(pz)$, 9.

	x[a]	y	z	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	23717(3)	124543(14)	37118(3)	535(4)	554(4)	607(4)	-53(4)	112(3)	54(4)
Cu2	18840(3)	70218(13)	42920(3)	492(4)	575(4)	585(4)	-82(4)	117(3)	26(4)
O1	2624(1)	9960(6)	4407(1)	51(2)	46(2)	51(2)	-8(2)	8(1)	6(2)
N1	3176(2)	14363(7)	3905(1)	56(2)	45(2)	50(2)	-7(2)	18(2)	2(2)
N2	2229(2)	5481(7)	4994(1)	51(2)	41(2)	58(2)	-4(2)	23(2)	3(2)
N3	1614(2)	10565(8)	3366(2)	57(2)	58(3)	63(3)	-3(2)	4(2)	9(2)
N4	1412(2)	8318(7)	3610(1)	51(2)	55(3)	62(2)	-3(2)	7(2)	1(2)
N5	4090(2)	18214(9)	2575(2)	89(3)	79(3)	64(3)	-4(3)	27(2)	-5(3)
N6	1383(2)	1473(10)	6244(2)	94(3)	90(4)	83(3)	-7(3)	31(3)	5(3)
C1	3161(2)	10007(8)	4783(2)	48(2)	41(3)	49(3)	-1(2)	14(2)	-6(2)
C2	3667(2)	11901(8)	4760(2)	47(2)	44(3)	50(2)	-4(2)	16(2)	-3(2)
C3	3633(2)	13920(9)	4330(2)	54(3)	46(3)	57(3)	-9(2)	22(2)	-10(2)
C4	4231(2)	11854(9)	5181(2)	45(2)	54(3)	65(3)	-4(2)	16(2)	-6(3)
C5	4326(2)	10099(10)	5624(2)	45(2)	65(3)	54(3)	-1(2)	10(2)	-7(3)
C6	4942(3)	10164(16)	6072(3)	55(3)	113(5)	78(4)	-5(3)	-2(3)	4(4)
C7	3833(2)	8315(10)	5645(2)	54(3)	61(3)	48(3)	1(2)	15(2)	1(2)
C8	3249(2)	8178(8)	5237(2)	45(2)	47(3)	46(2)	-5(2)	13(2)	-3(2)
C9	2784(2)	6107(9)	5313(2)	57(3)	54(3)	49(3)	3(2)	20(2)	5(2)
C10	868(2)	7395(12)	3265(2)	58(3)	74(4)	74(3)	-13(3)	5(3)	-4(3)
C11	719(3)	8962(12)	2806(2)	61(3)	90(4)	66(3)	1(3)	-7(3)	-6(3)
C12	1187(3)	10881(11)	2876(2)	76(3)	67(4)	67(3)	2(3)	0(3)	6(3)
C13	3289(3)	16574(9)	3531(2)	73(3)	44(3)	57(3)	-8(2)	22(2)	0(2)
C14	3398(3)	15393(11)	2997(2)	124(5)	56(3)	76(4)	-9(3)	47(3)	2(3)
C15	3480(2)	17556(10)	2591(2)	86(3)	55(3)	51(3)	-9(3)	23(3)	-6(3)
C16	2955(3)	18762(13)	2257(2)	83(4)	85(4)	72(4)	-11(3)	22(3)	-14(3)
C17	3054(3)	20797(13)	1894(2)	114(5)	87(4)	53(3)	16(4)	2(3)	-5(3)
C18	3670(4)	21466(12)	1877(2)	148(6)	72(4)	60(3)	-7(4)	43(4)	0(3)
C19	4166(3)	20198(13)	2217(3)	92(4)	85(4)	80(4)	-20(4)	37(3)	-8(4)
C20	1866(2)	3367(9)	5219(2)	56(3)	50(3)	62(3)	-9(2)	22(2)	4(2)
C21	1377(3)	4646(11)	5507(3)	71(3)	63(3)	99(4)	6(3)	45(3)	7(3)
C22	1030(2)	2604(10)	5789(2)	60(3)	62(3)	75(3)	-7(3)	35(3)	-5(3)
C23	392(3)	2021(13)	5593(2)	63(3)	106(5)	87(4)	-4(4)	27(3)	0(4)
C24	98(3)	119(17)	5871(3)	77(4)	147(7)	131(6)	-45(5)	46(4)	-36(6)
C25	443(4)	-1058(15)	6319(3)	136(6)	114(6)	119(6)	-39(5)	85(5)	-11(5)
C26	1070(4)	-366(14)	6499(3)	145(6)	94(5)	77(4)	0(5)	44(4)	14(4)

	x	y	z	B, Å^2		x	y	z	B, Å^2
H3	401(2)	1530(8)	438(2)	5.00	H14'	378(2)	1416(10)	310(2)	7.20
H4	451(2)	1324(8)	517(2)	5.10	H16	256(2)	1839(9)	228(2)	7.00
H6	502(2)	1180(10)	623(2)	8.00	H17	268(2)	2170(9)	166(2)	7.70
H6'	529(2)	1008(11)	595(2)	8.00	H18	376(2)	2302(9)	166(2)	7.30
H6''	495(2)	864(10)	628(2)	8.00	H19	460(2)	2057(9)	224(2)	7.40
H7	385(2)	693(8)	592(2)	5.00	H20	215(2)	213(8)	548(2)	5.30
H9	291(2)	506(8)	565(2)	5.10	H20'	164(2)	216(8)	493(2)	5.30
H10	69(2)	577(9)	338(2)	6.10	H21	108(2)	554(9)	522(2)	6.30
H11	38(2)	879(9)	253(2)	6.60	H21'	156(2)	587(9)	577(2)	6.30
H12	125(2)	1252(9)	268(2)	6.70	H23	15(2)	295(9)	527(2)	7.00
H13	362(2)	1758(8)	371(2)	5.40	H24	-36(2)	-46(10)	573(2)	9.10
H13'	288(2)	1786(8)	346(2)	5.40	H25	25(2)	-242(10)	652(2)	8.50
H14	298(2)	1442(10)	283(2)	7.20	H26	135(2)	-113(10)	682(2)	9.10

[a] Fractional coordinates have been multiplied by factors of 10^5 for the copper atoms, 10^4 for the remaining nonhydrogen atoms, and 10^3 for the hydrogen atoms. U_{ij} has been multiplied by 10^4 for the copper atoms and 10^3 for the remaining nonhydrogen atoms. [b] The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2}+\cdots+2U_{23}klb^*c^*)]$ for the anisotropic thermal parameters.

Table V. Bond Distances (Å) for $Cu(I)_2$ISOIM$(Etpy)_2(pz)$, 9.

Cu1-O1	2.089 (2)	C16-C17	1.391 (8)
Cu1-N1	1.901 (3)	C17-C18	1.344 (8)
Cu1-N3	1.882 (3)	C18-C19	1.345 (9)
Cu2-O1	2.097 (2)	C20-C21	1.508 (7)
Cu2-N2	1.894 (3)	C21-C22	1.499 (7)
Cu2-N4	1.878 (3)	C22-C23	1.354 (7)
O1-C1	1.300 (4)	C23-C24	1.385 (9)
N1-C3	1.281 (5)	C24-C25	1.322 (11)
N1-C13	1.482 (5)	C25-C26	1.339 (10)
N2-C9	1.296 (5)	C3-H3	1.03 (4)
N2-C20	1.469 (5)	C4-H4	0.90 (4)
N3-N4	1.372 (5)	C6-H6	0.90 (5)
N3-C12	1.355 (6)	C6-H6'	0.85 (5)
N4-C10	1.349 (6)	C6-H6''	0.90 (5)
N5-C15	1.330 (6)	C7-H7	0.96 (4)
N5-C19	1.353 (7)	C9-H9	0.96 (4)
N6-C22	1.331 (6)	C10-H10	0.95 (4)
N6-C26	1.354 (8)	C11-H11	0.88 (4)
C1-C2	1.424 (5)	C12-H12	0.96 (4)
C1-C8	1.421 (5)	C13-H13	0.89 (4)
C2-C3	1.449 (5)	C13-H13'	1.05 (4)
C2-C4	1.399 (5)	C14-H14	1.01 (5)
C4-C5	1.378 (6)	C14-H14'	0.99 (5)
C5-C6	1.513 (7)	C16-H16	0.87 (4)
C5-C7	1.366 (6)	C17-H17	0.98 (5)
C7-C8	1.413 (5)	C18-H18	0.98 (4)
C8-C9	1.453 (6)	C19-H19	0.91 (5)
C10-C11	1.355 (7)	C20-H20	0.99 (4)
C11-C12	1.348 (7)	C20-H20'	0.97 (4)
C13-C14	1.507 (7)	C21-H21	0.95 (4)
C14-C15	1.501 (7)	C21-H21'	0.90 (4)
C15-C16	1.363 (7)	C23-H23	0.97 (4)
		C24-H24	0.99 (5)
		C25-H25	0.97 (5)
		C26-H26	0.96 (5)

Table VI. Bond Angles (deg.) for $Cu(I)_2ISOIM(Etpy)_2(pz)$, 9.

O1-Cu1-N1	91. 7 (1)	C4-C5-C6	121. 8 (4)
O1-Cu1-N3	97. 1 (1)	C4-C5-C7	116. 9 (4)
N1-Cu1-N3	167. 6 (2)	C6-C5-C7	121. 3 (4)
O1-Cu2-N2	91. 5 (1)	C5-C7-C8	123. 4 (4)
O1-Cu2-N4	96. 8 (1)	C1-C8-C7	118. 8 (4)
N2-Cu2-N4	170. 7 (2)	C1-C8-C9	124. 8 (4)
Cu1-O1-Cu2	104. 2 (1)	C7-C8-C9	116. 4 (4)
Cu1-O1-C1	127. 5 (3)	N2-C9-C8	129. 0 (4)
Cu2-O1-C1	127. 7 (3)	N4-C10-C11	110. 6 (5)
Cu1-N1-C3	126. 1 (3)	C10-C11-C12	105. 2 (5)
Cu1-N1-C13	117. 3 (3)	N3-C12-C11	110. 0 (5)
C3-N1-C13	116. 6 (4)	N1-C13-C14	109. 8 (4)
Cu2-N2-C9	125. 5 (3)	C13-C14-C15	112. 1 (5)
Cu2-N2-C20	120. 4 (3)	N5-C15-C14	116. 2 (4)
C9-N2-C20	114. 1 (4)	N5-C15-C16	122. 2 (5)
Cu1-N3-N4	120. 6 (3)	C14-C15-C16	121. 5 (5)
Cu1-N3-C12	133. 1 (3)	C15-C16-C17	119. 6 (5)
N4-N3-C12	106. 3 (4)	C16-C17-C18	118. 4 (6)
Cu2-N4-N3	121. 2 (3)	C17-C18-C19	119. 1 (6)
Cu2-N4-C10	131. 8 (3)	N5-C19-C18	124. 3 (6)
N3-N4-C10	107. 0 (4)	N2-C20-C21	110. 1 (4)
C15-N5-C19	116. 4 (4)	C20-C21-C22	112. 8 (4)
C22-N6-C26	115. 9 (5)	N6-C22-C21	116. 0 (4)
O1-C1-C2	121. 5 (4)	N6-C22-C23	123. 0 (5)
O1-C1-C8	120. 2 (4)	C21-C22-C23	121. 1 (5)
C2-C1-C8	118. 4 (4)	C22-C23-C24	118. 4 (6)
C1-C2-C3	124. 0 (4)	C23-C24-C25	119. 5 (7)
C1-C2-C4	118. 6 (4)	C24-C25-C26	119. 3 (7)
C3-C2-C4	117. 4 (4)	N6-C26-C25	123. 8 (7)
N1-C3-C2	129. 2 (4)		
C2-C4-C5	124. 0 (4)		

Table VII. Nonbonding Distances and Associated Angles for $Cu(I)_2ISOIM(Etpy)_2(pz)$, 9.

Cu1-Cu2 ‡	3.3036 (4)	Cu1-Cu2+	2.9685(4)
Cu1-H13' ‡	2.64 (4)	Cu2-H20' +	3.09 (4)
O1-Cu1-Cu2+	95.7 (1)	O1-Cu2-Cu1‡	105.5 (1)
N1-Cu1-Cu2+	83.2 (1)	N2-Cu2-Cu1‡	92.1 (1)
N3-Cu1-Cu2+	104.5 (1)	N4-Cu2-Cu1‡	89.6 (1)

+ Translated by one unit cell in positive y direction

‡ Translated by one unit cell in negative y direction

infinite stack in the direction of the b axis, a section of which is shown in Figure 5. Although the separation between molecules in the direction of the b axis is 4.929 Å (just the length of the b axis), the molecule is far from perpendicular to this axis, the angle between the axis and the mean molecular plane being 41°. Thus, "overlapping" portions of neighboring molecules come rather close to one another. The average distance of atoms O1, C1, C8, C9, and N2 from the mean plane of atoms N1, C3, C2, C1, and O1 in the neighboring molecule just below is 3.20 Å. This is somewhat shorter than the separation usually observed between stacked π-delocalized molecules.[19] The intermolecular copper-copper distance is shorter yet, at 2.968 Å.

A least squares plane calculation including the atoms of the benzene ring, the methyl carbon, and the phenolic oxygen shows these atoms to be coplanar, with no deviation from the mean plane exceeding 0.009 Å. The deviations of the copper atoms from this plane are 0.04 Å for Cu1 and 0.29 Å for Cu2. In each case the direction of the out-of-plane separation is that which reduces the intermolecular copper-copper distance. Each of the two C=N groups is also twisted slightly out of plane in the direction of the copper atom to which it is bound (deviations: 0.04 Å for C3, 0.05 Å for N1, 0.04 Å for C9 and 0.10 Å for N2).

The atoms of the pyrazolate group are coplanar with no deviation from the mean plane exceeding 0.006 Å. The benzene and pyrazole rings are not quite coplanar, the dihedral angle being 170(3)°.

There is also a slight deviation of each copper atom from the plane defined by the three atoms to which it is bound. These deviations

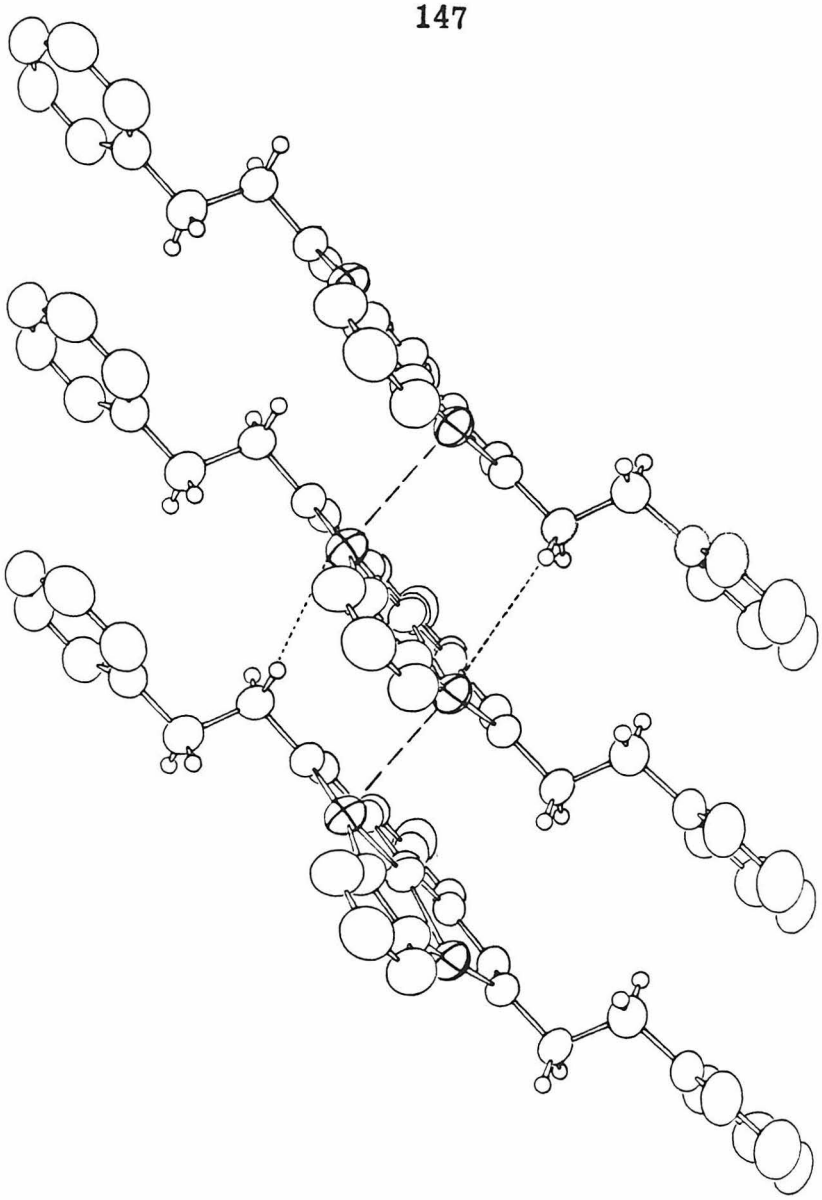


Figure 5. Crystal packing of Cu^{I}_{2}ISOIM(Etpy)$_2$(pz), 9, showing a section of an infinite stack of molecules which forms in the solid state. The three molecules are corresponding ones from three different unit cells, translated along the b axis (which lies in the vertical direction in the orientation of this figure). All copper atoms lie in the same plane, parallel to the page. The pyrazolate groups are directed out of the page, toward the reader. The shortest copper-copper distance, 2.97 Å, occurs between atoms in neighboring molecules, connected by dashed lines in the figure. The two dotted lines correspond to two different intermolecular Cu-H distances, 2.64 Å (Cu1-H13′) and 3.09 Å (Cu2-H20′).

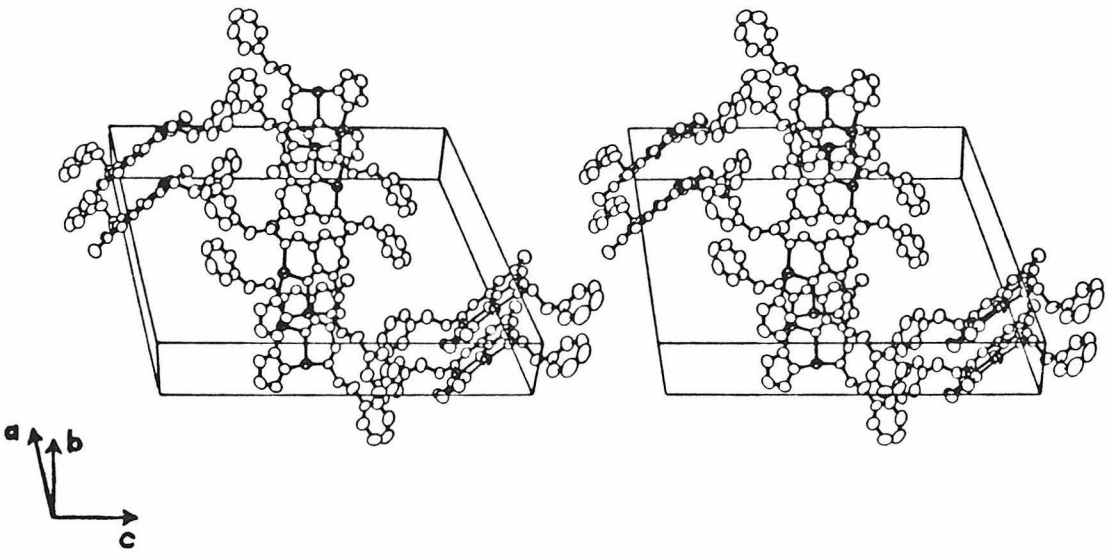


Figure 6. Stereoview illustrating crystal packing of Cu^{I}_{2}ISOIM(Etpy)$_2$(pz), 9. The molecules depicted comprise more than one unit cell, although the edges of only one cell are shown.

are 0.14 Å for Cu1 and 0.06 Å for Cu2. Again, in each case the direction of the out-of-plane separation is that which reduces the intermolecular copper-copper distance.

It should be noted that a possible attraction for another copper atom is not the only factor favoring this direction for the out-of-plane separation. As shown in Figure 5, there is a hydrogen atom on the opposite side of each copper atom, and in the case of Cu1 this hydrogen is at a distance of 2.64 Å. (This is also the copper that is farther out of its donor-atom plane.) Thus, at least for Cu1, copper-hydrogen steric interactions may influence the out-of-plane displacement of the copper ion.

A final point which should be noted concerning the coordination about copper is that the copper-nitrogen bonds are shorter than most which have been reported for Cu(I) complexes with nitrogen donor ligands.[22] The average lengths are 1.88 Å for the copper-pyrazole nitrogen bonds and 1.90 Å for the copper-imine nitrogen bonds. The copper-oxygen distances are substantially longer than this, averaging 2.09 Å. Also, as stated previously, the N-Cu-N bond angles approach 180° (167.6° and 170.7°). These factors may suggest some degree of two-coordinate character, which may be related to the unusual chemical behavior of the compound (e.g., unreactivity toward CO).

Discussion

The rather negative reduction potentials observed for complex 1 (equations 1 and 2) likely result from a square-planar arrangement of "hard" oxygen and nitrogen ligands.[25] The complexes reported here

were designed to stabilize copper(I) in an attempt to better model binuclear copper protein sites. For example, the condensation of 2-hydroxy-5-methylisopthalaldehyde with 2-aminomethylpyridine resulted in the binucleating ligand in 3, which is more flexible than the ligand system in 1 and also presents relatively soft pyridines for coordination. Two additional binucleating ligands providing even greater flexibility were obtained using 2-(2'-aminoethyl)pyridine and histamine, and these ligands reacted readily with copper(II) salts to yield the binuclear copper(II) complexes 4, and 5. Complexes similar to 4 and 5 were reported during the course of the present study.[26]

In all three copper(II) complexes, both copper atoms are presumably bound to an aromatic nitrogen. This has been demonstrated by an X-ray structure determination of $Cu_2^{II}ISOIM(hist)_2(OH)^{2+}$, 5.[27] Each copper(II) is actually five-coordinate with one of the copper atoms bound to the oxygen of a water molecule and the other copper bound to the oxygen of the hydroxy bridge of an adjacent molecule.

The electrochemistry of these non-macrocyclic complexes, 3-5, is irreversible as shown in Figure 3 for $Cu_2^{II}ISOIM(Mepy)_2(OH)^{2+}$, 3. This may be a result of the relatively labile hydroxy bridge, which is a poor ligand for copper(I). The introduction of pyrazole did produce reversible electrochemical behavior, also shown in Figure 3, leading to the isolation of a stable binuclear copper(I) complex, $Cu_2^{I}ISOIM-(Mepy)_2(pz)$, 6, by constant potential electrolysis (n = 2).[17] The reduction potentials observed for $Cu_2^{I}ISOIM(Mepy)_2(pz)$, 6, ($E_1^f$ = -0.21 V, E_2^f = -0.45 V) were appreciably more positive than those observed for the macrocyclic complex, 1, indicating that the binucleating ligand in

6 does indeed provide a better environment for copper(I) relative to copper(II).

The copper(I) compound Cu_2^{I}ISOIM(Mepy)$_2$(pz), 6, was also synthesized directly from cuprous starting materials. Similar reactions with 2-aminomethylpyridine or 2-(2′-aminoethyl)pyridine as sidearms and with pyrazole, 3,5-dimethylpyrazole or 7-azaindole as bridging ligands gave complexes 7-11. The coordination environment around each copper(I) of these complexes was expected to be a tetrahedral arrangement of one oxygen and three nitrogen ligands. The crystallographic results presented herein for Cu_2^{I}ISOIM(Etpy)$_2$(pz), 9, did not yield the expected structure. The sidearm pyridine nitrogen atoms are <u>not</u> coordinated. The overall coordination about copper approximates trigonal pyramidal, with a long, axial, copper-copper interaction with Cu^{I}-Cu^{I} = 2.97 Å. Copper(I)-copper(I) interactions with metal separations as short as 2.45 Å are known, but in all previously characterized species having proposed Cu^{I}-Cu^{I} interactions there is at least one bridging ligand between the two interacting copper atoms.[28] It is reasonable to assume that the structures of the analogous species, 6-11, are similar to this structure found for Cu_2^{I}ISOIM(Etpy)$_2$(pz), 9.

The structure of Cu_2^{I}ISOIM(Etpy)$_2$(pz), 9, suggested the synthesis of a series of compounds which had <u>no</u> donor atoms on the sidearms (R), <u>i.e.</u>, complexes 12-25, Table I. These compounds also proved to be crystalline compounds, stable in the absence of dioxygen. Since the polydentate ligand systems employed provide only three-coordination for each copper, these compounds are presumed to be three-coordinate in solution.

All compounds which have non-bulky sidearms are brown in the solid state, this color being due, in part, to a 600 nm band observed in the solid state nujol mull spectrum (Curve A in Figure 1). This band is not present in the spectrum of the complex with t-butyl sidearms, Cu_2^IISOIM(t-Bu)$_2$(pz), 20, which is red in the solid state as well as in solution (Curve C, in Figure 1). This 600 nm band may be attributed to the intermolecular copper-copper interaction which may be inhibited by the presence of large t-butyl sidearms. This copper-copper interaction appears to be only a solid state phenomenon, since the 600 nm band was not found in solution spectra, even in very concentrated solutions.

This novel dimerization of d^{10} copper(I) centers may be closely related to the dimerization observed for rhodium(I), d^8, isocyanide complexes.[29] The intermolecular bonding of $Rh(CNPh)_4^+$ monomers results from the mixing of higher energy orbitals with the lower energy (filled) d orbitals, resulting in overall stabilization. These bonding interactions give rise to an electronic absorption at lower energy than the original monomer transition. Similarly, the 600 nm absorption observed in the solid state for Cu_2^IISOIM(EtPh)$_2$(pz), 15, is lower in energy, compared to the 440 nm absorption observed for the same compound in solution (Figure 1). Note that in the solid state, the higher energy band is at 460 nm. This shift from solution to solid state and the asymmetric nature of the 440 nm solution band suggest that this solution absorption is due to several transitions, one of which may be shifted to lower energy (600 nm) upon interaction with another copper(I). Complexes with apparent copper(I)-copper(I) interactions

have not been reported to exhibit notable electronic absorption spectra. Exact assignments of the electronic absorption spectral bands in the copper(I) complexes reported herein await further studies.

The solution structure of $Cu_2^{I}ISOIM(Etpy)_2(pz)$, 9, appears to be similar to that found in the solid state with the absence of the intermolecular Cu-Cu interaction. The pyridine nitrogens do not appear to be bound in benzene solution, since the NMR resonance for the proton on the carbon adjacent to the pyridine nitrogen (py_1, Table I) of $Cu_2^{I}ISOIM(Etpy)_2(pz)$, 9, occurs at the same position, within experimental error, as the corresponding proton from 2-(2'-aminoethyl)-pyridine (i.e., 8.44 ± 0.02 ppm δ from TMS). In fact, all compounds which contain pyridine on the sidearms exhibit this resonance at the same position within experimental error (i.e., 8.42 ± 0.04 ppm δ from TMS). The resonance of this proton would be expected to shift downfield upon binding to a copper(I) ion. This effect has been observed for the proton in the 2 position of an imidazole ring, which shifts by 0.4 - 0.7 ppm downfield upon binding copper(I) to the imidazole ring.[30] Sharp resonances were observed for the pyrazole protons of these compounds (for instance, the doublet at 7.87 ppm and the triplet at 6.43 ppm in Figure 2). This indicates that there is no equilibrium between bound and unbound pyrazole, and hence the pyrazolate bridge must be totally bound to the copper(I) ions or totally dissociated in benzene solutions (unlikely, at best). The 7-azaindolate bridge also appears to be completely bound to the copper ions in benzene solutions, since the resonances for the β_2 aliphatic hydrogens (on the sidearms) are split by the unsymmetric bridge (for instance, compound 22 in

Table I). Also, the resonances found for the 7-azaindolate protons are very sharp peaks, indicating that no dissociation equilibrium is occurring.

The new copper(I) compounds serve as an interesting series for electrochemical comparisons. Several trends can be observed in Table II. In the following discussion, the formal potentials for the second reduction, (E_2^f), equation 4, will be used since these processes

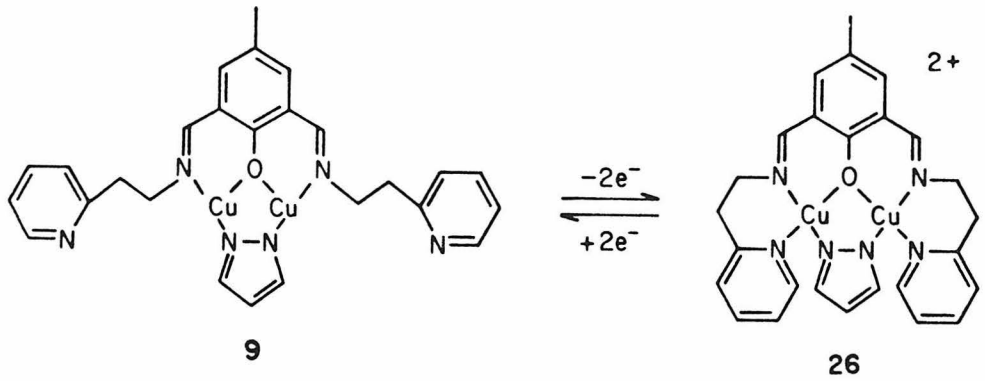
$$Cu^{II}Cu^{I}L^{+} + e^{-} \overset{E_2^f}{\rightleftharpoons} Cu^{I}Cu^{I}L \qquad (4)$$

were more reversible and slightly more systematic than the E_1^f potentials. The general trends, however, are the same with both processes.

The first point of interest is the effect of possible binding sites (i.e., pyridine) in the sidearms. The following series of potentials (E_2^f) was observed: Cu_2^IISOIM(EtPh)$_2$(pz), 15, (-0.078 V) $\approx$ Cu_2^IISOIM(MePh)$_2$(pz), 12, (-0.081 V) $\gg$ Cu_2^IISOIM(Etpy)$_2$(pz), 9, (-0.344 V) $>$ Cu_2^IISOIM(Mepy)$_2$(pz), 6, (-0.452 V). This indicates that the complexes containing the pyridine rings provide a more favorable environment for copper(II) relative to copper(I) when compared to their benzene ring analogues. Since the pyridine nitrogens do not appear to be bound to the copper(I) ions (in solution or in the solid state), the effect of these pyridine rings must be largely on the oxidized copper(II) sites. Hence, it appears that the pyridines bind to the copper ions upon oxidation, 26, and dissociate from copper(I) upon reduction, 9, Scheme III. Recall that in the similar cupric complex,

$Cu_2^{II}ISOIM(hist)_2(OH)^{2+}$, 5, the imidazole nitrogens were shown to be coordinated in the solid state X-ray structure.[27] It is reasonable that sidearm pyridine nitrogens would also coordinate to copper(II). The above series also indicates that the methyl pyridine sidearm provides a better environment for copper(II) than does the ethyl pyridine sidearm. This may be a result of the geometry of the sidearms and their relative ability to bind to the copper(II) centers.

Scheme III.



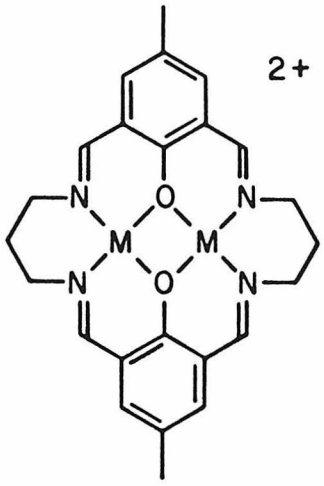
9 26

The introduction of methyl substituents on the pyrazolate bridges causes an increase in the reduction potential (E_2^f) as follows: $Cu_2^{I}ISOIM(Mepy)_2(Me_2pz)$, 7, (-0.374 V) > $Cu_2^{I}ISOIM(Mepy)_2(pz)$, 6, (-0.452 V) and $Cu_2^{I}ISOIM(MePh)_2(Me_2pz)$, 13, (+0.005 V) > $Cu_2^{I}ISOIM(MePh)_2(pz)$, 12, (-0.081 V). An inductive effect of the methyl groups would stabilize copper(II) relative to copper(I), but the reverse trend is actually observed. The steric bulk of the methyl

groups may be responsible for the relative destabilization of copper(II). These methyl groups may inhibit the binding of both pyridine (from the sidearms) and DMF (solvent) to the oxidized copper(II) ions by partially blocking the fourth, square-planar binding site around each copper(II). Also, shielding the copper centers from the solvent molecules with hydrophobic groups (such as these methyls) may not allow the polar DMF molecules to efficiently solvate the charged copper(II) species. Relative stabilization of copper(I) also results from more bulky sidearms, as reflected in the following series (E_2^f): Cu_2^IISOIM(t-Bu)$_2$(pz), 20, (+0.053 V) > Cu_2^IISOIM(2-Pr)$_2$(pz), 19, (+0.001 V) > Cu_2^IISOIM(1-Pr)$_2$(pz), 18, (-0.076 V).

Finally, an electronic effect on E_2^f is observed in the series of compounds which have phenyl rings bonded directly to the imine nitrogens: Cu_2^IISOIM(PhCOMe)$_2$(pz), 25, (+0.008 V) > Cu_2^IISOIM(Ph)$_2$(pz), 23, (-0.032 V) > Cu_2^IISOIM(PhNMe$_2$)$_2$(pz), 24, (-0.048 V). Here, the electron withdrawing carbonyl substituent results in relative copper(II) stabilization. Similar effects of remote substituents have been reported recently for a series of mononuclear copper(II) complexes.[10]

The oxidation/reduction of these compounds in two one-electron steps was the expected behavior for two interacting metal centers.[14,32] This sequential behavior has been observed for the series of binuclear complexes, 27, recently investigated in our laboratories.[33] Stepwise oxidation/reduction was also found for many ruthenium(II) dimers, in which closer proximity and greater interactions between the ruthenium centers correlates with a greater separation of the two redox



M = Mn, Fe, Co, Ni, Cu

27

processes (and larger comproportionation constants).[34] That all the new complexes exhibit two one-electron redox waves further suggests that the binuclear compounds are monomeric in solution. Oligomerization would probably result in intermolecular copper-copper interactions leading to more complex electrochemical behavior. Even the complexes with t-butyl sidearms, which were designed to inhibit intermolecular interactions, show electrochemical behavior similar to all other compounds. It thus seems likely that all new complexes have comparable solution structures, the most probable having three-coordinate copper(I).

The average comproportionation constant found for the binuclear copper complexes in this study (from Table II) was $K = 1.9 \times 10^3$, which is smaller than that found for the macrocyclic binuclear copper complex, 1 ($K = 4 \times 10^6$).[14] This is reasonable since the lower value was observed for the present copper(I) compounds which contain one

pyrazolate type bridge and one phenoxide bridge, compared to two phenoxide bridges between the coppers in 1. The pyrazolate bridge is expected to result in a larger Cu-Cu distance and smaller intramolecular copper interactions. The oxidized binuclear copper(II) complexes with bridging pyrazolate, such as 26, Scheme III, were not isolated in the present study, but the relative effects of alkoxide vs. pyrazolate bridges on metal interactions have been demonstrated in similar binuclear copper(II) compounds, and the trend was the same as found here.[35]

The non-reactivity of the copper(I) complexes in the present study toward carbon monoxide is an addition to the confusing phenomenon of carbon monoxide binding to copper(I) complexes. In general, copper(I) complexes have been found to bind CO if a fourth coordination site is available.[12,31,36] On the other hand, most four-coordinate copper(I) compounds do not bind CO, with the exception of several square-planar, four-coordinate complexes which bind CO as a fifth ligand.[13-15] Obviously, the geometry and type of ligands around copper(I) affect the CO binding ability for copper(I). The nature of these effects, however, remains obscure.

Biological Implications

It may not be valid to compare exact reduction potentials of simple metal complexes with those of corresponding protein systems due to varying solvation effects.[37] Nonetheless, analysis of trends or comparisons of approximate potentials may be useful. Within this context the high reduction potentials observed for binuclear copper

protein sites have been "mimicked" by the binuclear copper complexes presented in this study. Hence, it is not unreasonable to believe that these proteins utilize only oxygen and/or nitrogen ligands around each copper. Indeed, a three-coordinate copper-ligand environment can be considered for the reduced form of the binuclear site. The non-reactivity of the new compounds towards CO is in contrast to hemocyanin. This does not preclude a three-coordinate reduced binuclear site, since some three-coordinate copper(I) complexes have been shown to bind CO.[12,31,36]

The oxidation/reduction of these compounds in well separated one-electron steps, contrasts with the available electrochemical information on the binuclear protein sites. While no electrochemical data are available on hemocyanin, for both laccase and tyrosinase, a single potential has been associated with the overall two-electron reduction of the binuclear copper site.[6,7,38] Correlations between the electrochemical behavior of the new compounds, 6-25 and of the proteins is difficult due to solvation effects, the different techniques employed, possible non-equilibria in the proteins, etc.[37,38] Nonetheless, the electrochemical behavior reported for the new compounds suggests that the two-electron reduction of laccase and of tyrosinase is probably not a simple reduction of two equivalent copper ions strongly interacting through bridging ligands.

Conclusions

Stable binuclear copper(I) complexes have been prepared using binucleating ligands. Several of the new complexes exhibit copper-copper interactions in the solid state, as suggested by a peculiar visible absorption spectrum. This was confirmed for Cu_2^IISOIM-(Etpy)$_2$(pz), 9, via a complete molecular structure determination. In addition to the copper-copper interaction each copper(I) is bound to one oxygen and two nitrogen ligands. In solution all the new cuprous complexes likely contain three-coordinate copper, which appears to be a quite stable environment for copper(I).

All new complexes exhibit two one-electron redox processes, at well defined potentials. The highest reduction potentials were observed for complex 21 in which the copper(I) centers are somewhat buried within the hydrophobic substituents. With reduction potentials of E_1^f = 0.239 V and E_2^f = 0.080 V, the ligand environment in 21 represents a substantial improvement on the original square-planar, four-coordinate ligand environment provided by the starting model, 1. The reason for this high (relative) stability of copper(I) within the new molecules is not obvious. While many three-coordinate mononuclear copper(I) complexes have been isolated employing very soft phosphorous or sulfur donors, very few three-coordinate mononuclear (or binuclear) copper(I) complexes have been isolated with nitrogen or oxygen donors.[23,28,39] The binuclear nature of the compounds in this study may be responsible for their stability. Perhaps the second copper serves to anchor the binucleating ligands, promoting a favorable three-

coordinate environment around each copper(I).

Relatively high reduction potentials on the order exhibited by these complexes (and by the binuclear protein site) may be necessary for reversible oxygen binding.[40] Unfortunately these complexes have thus far reacted irreversibly towards oxygen. We are presently investigating modifications on the sidearms and their effect on the nature of the oxygenation reaction.

Acknowledgment. We appreciate helpful discussions from T. J. Smith and financial assistance from the National Institutes of Health (Grant No. PHS AM 18319-04) and the International Copper Research association.

Experimental Section

Materials. All chemicals were reagent grade and were used as received unless otherwise noted. Copper(II) tetrafluoroborate, ground to a powder then dried for several days in vacuo (25° C), was used as $Cu(BF_4)_2 \cdot 6H_2O$. Tetrabutylammonium perchlorate, TBAP, (Southwestern Analytical Chemicals) was dried exhaustively in vacuo (25° C) before use. Reagent grade N,N-dimethylformamide, DMF, was dried over $MgSO_4$ and 4A molecular sieves for 24 hours and then vacuum distilled. 2-Hydroxy-5-methylisophthalaldehyde was prepared by a modification of the literature method.[41] Tetra(acetonitrile) copper(I) tetrafluoroborate was also prepared by the published method.[42]

$Cu_2^{II}ISOIM(Mepy)_2OH(BF_4)_2 \cdot CH_3OH \cdot H_2O$, 3. Aminomethylpyridine (0.44 ml, 4 mmoles) was added to a solution of 2-hydroxy-5-methylisophthalaldehyde (0.33 g, 2 mmoles) in methanol (50 ml). The resulting yellow solution was boiled at reflux for 1 hour, after which, $Cu(BF_4)_2 \cdot 6H_2O$ (1.38 g, 4 mmoles) was added. This resulting blue-green solution was refluxed for 45 minutes. Removal of the solvent (methanol) using a rotary evaporator gave a blue-green solid, which upon recrystallization from methanol yielded blue-green crystals of 3. These crystals were washed with methanol followed by diethylether and dried under vacuum for several hours. Anal. ($C_{22}H_{26}N_4O_4Cu_2B_2F_8$), C, H, N, Cu.

$Cu_2^{II}ISOIM(Etpy)_2OH(BF_4)_2 \cdot CH_3CH_2OH$, 4. 2-(2'-Aminoethyl)-pyridine (0.50 ml, 4 mmoles) was added to a solution of 2-hydroxy-5-methylisophthalaldehyde (0.33 g, 2 mmoles) in ethanol (25 ml). The

resulting yellow solution was boiled at reflux for 5 min., and then $Cu(BF_4)_2 \cdot 6H_2O$ (1.38 g, 4 mmoles) was added to give a green solution. After boiling for 5 min., this solution was allowed to cool slowly to 4° C, and the resulting blue-green solid was collected and recrystallized from ethanol to give blue-green crystals of 4. The product was washed with ethanol, followed by diethyl ether and dried under vacuum for several hours. Anal. ($C_{25}H_{30}N_4O_3Cu_2B_2F_8$) C, H, N; Cu: Calcd, 17.3; Found 18.0.

Cu_2^{II}ISOIM(hist)$_2$OH$(BF_4)_2 \cdot H_2O$, 5. Histamine (0.44 g, 4 mmoles) was added to a solution of 2-hydroxy-5-methylisophthalaldehyde (0.33 g, 2 mmoles) in methanol (50 ml). The resulting yellow-orange solution was boiled at reflux for 15 min., and then $Cu(BF_4)_2 \cdot 6H_2O$ (1.38 g, 4 mmoles) was added to give a green solution. The solution was reduced to a small volume (~10 ml) using a rotary evaporator, and the resulting green solid was collected by vacuum filtration. Recrystallization of this solid from ethanol gave light blue-green needles of 5. The product was collected and washed with ethanol followed by diethylether, and then dried in vacuo for several hours. Anal. ($C_{19}H_{24}N_6O_3Cu_2B_2F_8$) C, H, N; Cu; Calcd 18.6; Found 19.3.

Cuprous Compounds. The series of copper(I) compounds 6-25 were synthesized in the manner described below for Cu_2^{I}ISOIM$(Etpy)_2(pz)$, 9, with the following modifications. The appropriate amine (RNH_2) and bridge (XH) were used to provide the R and X groups listed in Table I. The initial imine condensation is slow for the aromatic amines, and the amine and dialdehyde were allowed to react overnight, in refluxing

acetonitrile, in the synthesis of 23-25. Compounds 7, 10, 13, 16, and 23-25 were recrystallized with DMF instead of CH_3CN. Compounds 20-22 were recrystallized from heptane instead of acetonitrile.

$Cu_2^{I}ISOIM(Etpy)_2(pz)$, 9. The following was performed under helium in a Vacuum Atmospheres Dri-Lab inert atmosphere chamber. 2-(2'-Aminoethyl)pyridine (0.24 ml, 2 mmoles) was added to a solution of 2-hydroxy-5-methylisophthalaldehyde (0.16 g, 1 mmole) in acetonitrile (15 ml). The resulting yellow solution was heated at reflux for 15 min., and then cooled to the ambient temperature. Pyrazole (0.07 g, 1 mmole) and sodium methoxide (0.11 g, 2 mmole) were added to the solution, and after stirring briefly $Cu(CH_3CN)_4BF_4$ (0.63 g, 2 mmoles) was added to give a brown solution and a brown precipitate. This mixture was boiled at reflux for 15 min., and then the acetonitrile was removed by evaporation under vacuum. The brown solid was dissolved in hot toluene (30 ml), leaving behind a white solid ($NaBF_4$) upon vacuum filtration. The toluene was then removed from the filtrate by evaporation under vacuum to yield a brown solid. Recrystallization from acetonitrile gave brown needles, 9. The product was collected by vacuum filtration, washed with acetonitrile and dried for several hours in vacuo. Anal. ($C_{26}H_{26}N_6OCu_2$) C, H, N, Cu.

Physical Measurements. Sample preparation for physical studies on the air-sensitive materials was accomplished in a Vacuum Atmospheres Dri-Lab inert atmosphere chamber, under a helium atmosphere. Helium-saturated spectroquality solvents were used for solution studies.

Magnetic susceptibility measurements were done on powdered samples at the ambient temperature using a Cahn Instruments Faraday balance. The calibrant utilized was $HgCo(SCN)_4$, and diamagnetic corrections were made using Pascal's constants.

Electronic spectra were recorded on a Cary 14 spectrophotometer. Solid state spectra were obtained from Nujol mulls on filter paper against a Nujol-saturated filter paper as a blank.

Infrared spectra were recorded on a Beckman IR-12 Infrared Spectrophotometer. Solid state spectra were obtained from Nujol mulls pressed between KBr plates. Solution spectra were obtained using calcium fluoride solution cells (path length of 1 mm).

Proton magnetic resonance spectra were recorded on a Varian EM390 spectrophotometer at 90 MHz (34° C). The solvent utilized was d^6-benzene containing TMS as the reference.

Mass spectra and elemental analyses were performed by the Caltech Microanalytical Laboratory.

Electrochemistry. A Princeton Applied Research (PAR) Model 174A polarographic analyzer was used for cyclic voltammetry and differential pulse voltammetry. For display purposes, a Hewlett-Packard 7004B X-Y recorder was utilized. The apparatus used for constant potential electrolysis (cpe) consisted of a PAR Model 173 potentiostat-galvanostat coupled with a Model 179 digital coulometer.

Cyclic voltammetry was done in a single compartment cell with a volume of ca. 5 ml. In all solvents the supporting electrolyte was 0.1 M TBAP. The working electrode consisted of a platinum button electrode or a hanging mercury drop electrode. In all cases, the

auxiliary electrode was a coiled platinum wire, and the reference electrode consisted of a silver wire immersed in an acetonitrile solution containing $AgNO_3$ (0.01 M) and TBAP (0.1 M), all contained in a 9-mm glass tube fitted on the bottom with a fine porosity sintered glass frit. The apparatus employed for constant potential electrolysis was similar, except a two compartment H-cell was used to isolate the auxiliary electrode from the working compartment. A platinum gauze was used as the working electrode for cpe.

All potentials are reported versus the normal hydrogen electrode, nhe. This was accomplished by the use of an internal reference redox couple, namely ferrocene, for which the formal potential is reported to be +0.400 V versus nhe in water.[16] It has been proposed that the ferrocene reduction potential changes very little in different solvents, and hence it is a good solvent independent redox couple.[16] Experimentally, small amounts (ca. 10^{-3} M) of ferrocene were added to solutions containing the compounds of interest and formal potentials for both couples were measured under the same conditions.

X-Ray Data Collection and Reduction. Acicular crystals of 9 were grown by slow evaporation of an acetonitrile solution under helium. Preliminary oscillation and Weissenberg photographs showed the space group to be $P2_1/c$ (No. 14) uniquely defined by its extinctions.

A crystal of dimensions 0.04 mm × 0.08 mm × 0.33 mm (which had been cut from a larger needle) was mounted on a Syntex $P2_1$ four-circle diffractometer for data collection. No attempt was made to protect the crystal from atmospheric oxygen as no air sensitivity has been exhibited in the solid state. Cell parameters were determined

by a least-squares fit to fifteen automatically centered reflections with $2\theta > 56°$. The resulting parameters are given in Table III. Intensity data were collected from two octants using θ-2θ scans to a maximum 2θ of 130°. The scan range extended from 1° below the CuK_{α_1} 2θ value to 1° above the CuK_{α_2} value, and the scan rate was 1°/min, with the total background counting time equal to the total scan time. Three check reflections were measured after every fifty reflections to monitor the crystal and instrument stability.

Because the check reflections showed an overall drop in intensity of 5% during the course of data collection, the data were scaled in eleven groups according to the average intensity in each group of one of the check reflections (002). Lorentz and polarization corrections were then applied. Standard deviations of intensities were calculated using the formula

$$\sigma^2(I) = [S + (B1 + B2) + (dS)^2]/(Lp)^2,$$

where S, B1, and B2 are the scan and two background counts and d was taken as 0.02.[43] Absorption corrections were calculated by the method of gaussian quadrature.[44] After symmetry-extinct reflections were deleted and equivalent reflections averaged, there remained 4269 unique data ($3390 > 0$; a rather high percentage of the high 2θ data was "unobserved").

Solution and Refinment of the Structure. With the exception of C. K. Johnson's ORTEP program, all computer programs were from the CRYM system of crystallographic programs. Literature values were used for the scattering factors for Cu^+, O, N, and C,[45] the real

part of the anomalous dispersion correction for copper[45] and for the H scattering factors.[46] The function minimized in the least-squares refinement was $\Sigma_w(|F_o|^2 - |k' F_c|^2)^2$, where the weight $w = 1/\sigma^2(F_o^2)$, and F_o and F_c are the observed and calculated structure factors.

The positions of all nonhydrogen atoms were found using standard Patterson-Fourier techniques. Least-squares refinement with these atoms and isotropic temperature factors led to $R = \Sigma||kF_o|-|F_c||/\Sigma|kF_o| = 0.087$ (for those reflections with $F_o^2 > 2\sigma$). Use of anisotropic temperature factors for all nonhydrogen atoms lowered R to 0.062. The 26 hydrogen atoms were located by difference map techniques. Each was assigned a fixed isotropic temperature factor equal to 1.0 $Å^2$ greater than that for the carbon atom to which it was bound. Hydrogen positional parameters were refined. The final refinement was by blocked-matrix least-squares with all positional parameters in one matrix and the anisotropic thermal parameters and scale factor in another. No data were omitted from this refinement. The final R was 0.042 for the 2620 reflections with $F_o^2 > 2\sigma$; R for all data was 0.063. The final goodness of fit, $\Sigma w(k^2F_o^2 - F_c^2)^2/(n-p)$, was 2.85, where n = 4269 is the number of observations and p = 394 is the number of parameters. The largest feature in the final difference Fourier map was a peak of height 0.96 $eÅ^{-3}$, located approximately 0.7 Å from Cu2 in the positive y direction. The second highest peak (0.87 $eÅ^{-3}$) was not in a position of chemical significance (between the pyrazole groups of neighboring molecules). Final parameters and interatomic distances and angles are presented in Tables IV-VII.

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